

First Year BEng/MEng Mechanical/Aerospace Engineering

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Acknowledgements

The lecture notes presented herein are founded on an original set of lecture notes composed by Dr R. Prosser, School of Mechanical, Aerospace and Civil Engineering, University of Manchester.

Week	Teaching Week	Week Beginning	LECTURES Monday (4-5pm) Renold/C16	LECTURES Thursday (3-4pm) Renold/C16	TUTORIALS Thursday (9-10am)
1	19	22-Jan-18	Ch1: Basic Concepts	Ch1: Basic Concepts	-
2	20	29-Jan-18	Ch2: Work & Heat	Ch2: Work & Heat	Tutorial
3	21	05-Feb-18	Ch3: First Law	Ch3: First Law	-
4	22	12-Feb-18	Ch4: Pure Substances	Ch4: Pure Substances	Tutorial
5	23	19-Feb-18	Ch5: Open Systems	Ch5: Open Systems	-
6	24	26-Feb-18	Ch6: Gases	Ch6: Gases	Tutorial
7	25	05-Mar-18	Ch7: Heat Engines	Ch7: Heat Engines	-
8	26	12-Mar-18	Assignment (online quiz)	Review/Examples	Tutorial
9	27	19-Mar-18			
10	28	26-Mar-18			
11	29	02-Apr-18			
12	30	09-Apr-18	Ch8: Entropy	Ch8: Entropy	-
13	31	16-Apr-18	Ch8: Entropy	Ch8: Entropy	Tutorial
14	32	23-Apr-18	Review/Past Paper	Review/Past Paper	-
15	33	30-Apr-18	*Review/Past Paper	Review/Past Paper	Tutorial

TIMETABLE ARRANGEMENTS

* **NOTE:** This session is exceptionally scheduled for Thu 3 May 2018 @ 10-11am in C16 instead of the usual Monday 4-5pm)

COURSE MARKS

Balckboard based quiz (randomised multiple-choice questions)	20%
Final Examination (2 hrs)	80%

REQUIRED COURSE AND DATA BOOK

•	Thermodynamics-An Engineering Approach (SI Version) (8th Edition)	Cengel and Boles
•	Thermodynamic and Transport Properties of Fluids (5 th Edition) (<i>This book, also known as the 'steam table', is integral to the thermodynamics</i>	Rogers and Mayhew (~£10)
	modules this year and therefore each student must have access to a copy).	

INDICATIVE READING LIST:

•	Fundamentals of Thermodynamics (8 th ed.)	Borgnakke and Sonntag
•	Modern Thermodynamics-From Heat Engines to Dissipative Structures (2 nd ed.) <i>(rather advanced)</i>	Kondepudi and Prigogine
•	Introduction to Thermal Systems Engineering	Moran, Shapiro, Munson, DeWitt
•	Thermodynamics-for Engineers (2 nd ed., Schaum's outlines) (lots of solved problems and good value for money)	Potter and Somerton
•	Engineering Thermodynamics: Work and Heat transfer	Rogers and Mayhew
•	Applied Thermodynamics for Engineering Technologists	Eastop and McConkey
•	Introduction to Engineering Thermodynamics	Sonntag and Borgnakke
•	Thermodynamics for Dummies (£12/free eBook)	Pauken

DATA SHEETS FOR THERMODYNAMICS 1 (MACE11005)

1 Work

- positive work: is done by a system on the surroundings (a system does positive work if it can raise a weight)
- **negative work:** is done by the surroundings on a system.

Incremental piston, or displacement work , is $\delta W = p dV$, and for a process in which the pressure varies with volume the work is $W = \int p dV$

Constant pressure (isobaric) process: $pV^0 = c$

$$W_{12} = \int_{1}^{2} p dV = p \left(V_{2} - V_{1} \right)$$

Constant volume (isochoric) process: $pV^{\infty} = c$

$$V_{13} = \int p dV = 0$$
, because $dV = 0$

Process defined by pV = c

$$W_{14} = p_1 V_1 \ln \frac{V_4}{V_1} = p_1 V_1 \ln \frac{p_1}{p_4} = eta$$

Process defined by $pV^n = c$

$$V_{15} = \frac{p_1 V_1 - p_5 V_5}{n-1} = \frac{p_5 V_5 - p_1 V_1}{1-n}$$

2 First Law of Thermodynamics - closed systems

$$Q - W_s = m \left(u_2 + \frac{V_2^2}{2} + gz_2 \right) - m \left(u_1 + \frac{V_1^2}{2} + gz_1 \right)$$

First Law for a closed system in the absence of kinetic and potential energy $\delta Q = dU + \delta W$

Specific heat at constant volume

$$c_{v} = \left(\frac{\partial u}{\partial T}\right)_{v} = \left(\frac{\partial u}{\partial t}\right)_{v} = \left(\frac{\partial Q}{\partial T}\right)$$

H = U + pV

Enthalpy, H

Specific enthalpy, h

$$= \frac{H}{m} = \frac{U + pV}{m} = \frac{U}{m} + \frac{pV}{m} = u + pv$$

Specific heat at constant pressure

$$c_{p} = \left(\frac{\partial h}{\partial T}\right)_{p} = \left(\frac{\partial h}{\partial t}\right)_{p} = \left(\frac{\partial q}{\partial T}\right)_{p}$$

3 Steady flow energy equation

$$\dot{Q} = \dot{W} = \dot{h} \left(\dot{h}_{e} - \dot{h}_{i} + \frac{V_{e}^{2} - V_{i}^{2}}{2} + g(z_{e} - z_{i}) \right)$$

Stagnation enthalpy

$$h_0 = h + \frac{V^2}{2}$$

$$V_{2} = \sqrt{2} \left\{ \left(h_{1} - h_{2} \right) + \frac{V_{1}^{2}}{2} \right\}$$

Work from an adiabatic machine

$$W_{s} = \dot{m}(h_{e} - h_{i}) = \dot{m}(h_{2} - h_{1}).$$

4 Second Law of Thermodynamics

Velocity at exit to a nozzle

Efficiency

Useful work output Thermal efficiency , $\eta_{th} =$ Thermal energy input for a heat engine operating in a cycle Thermal efficiency of heat engine , $\eta_{th} = \frac{\text{Net work}}{\text{Heat supplied}}$ $\eta_{th} = \frac{W_s}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$ Thermal efficiency Coefficient of performance of refrigerator , $\beta = \frac{\text{Heat transferred from cold reservoir}}{\text{Work done}}$, $= \frac{Q_2}{W_s} = \frac{Q_2}{Q_1 - Q_2}$ Coefficient of performance Coefficient of performance of heat pump , $\beta' = \frac{\text{Heat transferred to hot reservoir}}{\text{Work done}}$, $= \frac{Q_1}{W_s} = \frac{Q_1}{Q_1 - Q_2}$. Coefficient of performance Relationship between coefficients of performance $\beta' = 1 + \frac{Q_2}{W_s} = 1 + \beta$ Entropy is denoted by the symbol - S; specific entropy is denoted by - s. Entropy The change of entropy between states 1 and 2 is $S_2 - S_1 = \int_{-\infty}^{2} \frac{\delta Q_R}{T}$ **Central Equation of Thermodynamics** Tds = du + pdv = dh - vdpSteady flow entropy equation for an adiabatic machine $S_i = \overline{m} \left(s_i - s_i \right) \ge 0$ **Properties of pure substances** Dryness fraction, or quality $v = xv_{g} + (1 - x)v_{f} = v_{f} + xv_{fg}$ $u = xu_{g} + (1 - x)u_{f} = u_{f} + xu_{fg}$, $x = \frac{\text{Mass of dry vapour}}{\text{Total mass of liquid}}$ Dryness fraction + vapour $h = xh_{g} + (1 - x)h_{f} = h_{f} + xh_{fg}$ $s = xs_{e} + (1 - x)s_{f} = s_{f} + xs_{fg}$ Perfect gases, and mixtures of perfect gases $\frac{pv}{T} = const$, R Ideal gas Universal Gas Constant, $\Re = MR$ S.I. units R = 8.3145 kJ/kmol K

$$\label{eq:mperial} \begin{split} \ensuremath{\mathfrak{R}} &= 1545 \mbox{ ft.lbf/lb mol }^{\circ}\mbox{R} \\ &= 1.986 \mbox{ Btu/lb mol }^{\circ}\mbox{R} \\ \ensuremath{\textbf{Molar Masses (kg/kmol) for Common Gases/Elements}} \\ \ensuremath{\mathsf{H}}_2:2 & O_2:32 & N_2:28 & CO:28 & CO_2:44 & H_2O:18 & C:12 \end{split}$$

Internal energy $u = \int_{T_o}^{T} c_v dT + u_o$, where u_0 is the value of u at temperature T_0 **Enthalpy** h = u + pv = u + RT $h = \int_{T_o}^{T} c_p dT + h_0$, where h_0 is the enthalpy at temperature T_0 .

Relationship between c_p and c_V

$$c_p = c_v + R$$

Entropy change

$$ds = \frac{c_v dT + p dv}{T} = c_v \frac{dT}{T} + \frac{p}{T} dv \quad , \quad s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T} dT + R \ln \frac{v_2}{v_1} \quad , \quad s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT - R \ln \frac{p_2}{p_1}$$

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CHAPTER 1

BASIC CONCEPTS

THE CHAPTER COVERS:

INTRODUCTION TO THE FOUR LAWS OF THERMODYNAMICS	Page 1.2
DEFINITION OF A SYSTEM	Page 1.3
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Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 1 "Introduction and Basic Concepts" pages 1-17.

CHAPTER 1: BASIC CONCEPTS IN THERMODYNAMICS

Introduction

Among the multitude of laws that described the workings of the universe there exists some whose importance transcends all others. The isolated phrase "the second law" is often sufficient information in itself to inform the intended audience that the second law of thermodynamics is meant. *Thermodynamics defines and describes the properties of energy and its transformation from one form to another.* Thus, thermodynamics is not simply about steam engines but applies to every aspect of physics invoking energy transport; put simply, it applies to all the sciences, be it chemical, electrical, mechanical, nuclear, and including natural sciences. As engineers we are often concerned with the analysis, workings and design of large scale systems such as power plants, heat engines, refrigerators, air conditioning, heat pumps etc. and consequently our focus (and the focus of thermodynamics) is on the *macroscopic* rather than the *microscopic* although an atomistic viewpoint (describable by *statistical mechanics*) can sometimes illuminate our conceptual understanding.

Thermodynamics is founded on just four laws:

- (i) The Zeroth Law establishes the familiar yet enigmatic property temperature T [K].
- (ii) The *First Law* establishes the property *internal energy* U [kJ].
- (iii) The Second Law establishes the (often considered recondite) property entropy S [kJ/K].
- (iv) The *Third Law* establishes a barrier that prevents the reaching of the temperature *absolute zero* [K].

The first and second laws are the most useful for practical purposes as they provide us with *transport equations* which can be applied to a moving/stationary *control volume*, which encompasses the thermodynamic *system*. The invariance of energy (in an *isolated system*) is the preserve of the first law but what energy changes are permitted is the preserve of the second.

Examples: of areas of application of thermodynamics in Mechanical Engineering

Power generation: a gas turbine for a power station



Propulsion: an aircraft gas turbine



Propulsion: a car engine



Definition of a System

Thermodynamics (as with the rest of science) takes familiar words and confers upon them an exact and unambiguous meaning.

- (i) A *system* is a collection of matter enclosed within a prescribed boundary.
- (ii) A *closed system* is a *system* distinguished by the absence of matter flowing across its boundary.
- (iii) An *open system* is a *system* distinguished by matter flowing across it boundary.
- (iv) A system is separated from its *surroundings* by a *boundary*. The boundary may be fixed or may move to contain the prescribed matter.
- (v) The *surroundings* are everything not contained within the system boundaries. The surroundings can often be considered vast, unaffected by the system (e.g. a bath of water, the atmosphere, the world, our solar system, the universe).
- (vi) An *isolated system* is a *system* distinguished by the absence of energy flowing across its boundary.
- (vii) A *control volume* is commonly used in the analysis of open systems and is typically defined to encompass the space occupied by an open system. The boundary of the control volume is denoted the *control surface* and matter is free to flow across this boundary.

The control volume concept coupled to their use with *transport equations* provides us with an extraordinarily powerful tool for analysis. All the classical conservation laws in physics can be described mathematically with *transport equations*, which relate the rate of change of an entity (e.g. mass, energy, entropy, etc.) in a control volume to the rate at which that entity passes through the control surface along with other transfer mechanisms.



Examples: Closed systems

The system is the air contained in a room with closed windows and doors. In this case the mass and volume of the system are constant.



The system is the air contained in the cylinder of an engine, and now the mass of the system is fixed but the volume varies as the piston moves.

Examples: Open systems



Schematic diagram of an open system showing a control volume and a control surface.

Schematic of a room with a door and window open: this constitutes an open system.





An internal combustion engine with the valves open is an open system.

Definition of a Property

A *property* of a system (in broad terms) is an *observable* characteristic; it can be subdivided into two categories; *external (mechanical)* and **internal (thermodynamic)**.

Typical mechanical properties are: velocity, height, kinetic energy, potential energy and momentum, and are measured relative to an external reference frame. These properties contain combinations of mass, position and time, which is sometimes denoted as the *mechanical co-ordinates* of the system although momentum, position and time are the most-favoured mechanical co-ordinates for reasons not discussed here.

Thermodynamic properties on the other hand are characteristic of the matter contained within a system **at equilibrium**. They are measured relative to an observer moving with the system and are sometimes denoted the *thermodynamic coordinates*. Common thermodynamic properties are: pressure, temperature, volume and quality but others occasionally considered are shape (surface effects) and colour (radiation heat transfer). An essential feature of a property is that it has a unique value when a system is in a particular *state* and that this value does not depend on previous states the system may have passed through. Thus a property is not dependent on *path* and this can be represented mathematically by the equation:

$$\int_{\phi_1}^{\phi_2} d\phi = \phi_2 - \phi_1$$

where ϕ is the property and ϕ_1 is the value of the property at state 1, ϕ_2 is the value at state 2 and $\phi_2 - \phi_1$ represents the change in the property as the system moves from state 1 to state 2.

The *state* of a system is its condition as described by giving values to its properties at a particular instant. The *two-property rule* states that the *state* of a *simple* (e.g. consisting of a pure substance) closed system of constant mass is defined by two *independent* properties. Pressure and volume are commonly used to define the state of a gas for example.

Thermodynamic properties can be further divided into *intensive*, *extensive* and *specific* properties. *Intensive* properties are independent of the mass (definable at a point) of the system (e.g. pressure, temperature, viscosity, thermal conductivity, etc.). *Extensive* properties depend on the mass (or extent) of the system and therefore apply to the whole system rather than at a point within the system (e.g. volume, surface area, mass, energy, enthalpy, entropy, etc.) **Specific** properties are a subclass of intensive properties obtained on division of extensive properties by the mass (e.g. specific volume, specific heat, specific enthalpy, etc.)

Properties can often be combined to form new properties. For example energy U [kJ], entropy S [kJ/K], pressure p [kPa], volume V [m³] and temperature T [K] can be combined to give for example *enthalpy* H = U + pV [kJ], *Helmholtz free energy* F = U - ST [kJ] and *Gibb's free energy* G = H - ST [kJ]. Dividing through by mass m gives specific entities (lower case used in this case): specific enthalpy h = u + pv [kJ/kg], specific Helmholtz free energy f = u - sT [kJ/kg] and specific Gibb's free energy g = h - sT [kJ/kg].

Formally: A property is any quantity whose change is fixed by the end states, and is independent of the path between the end states.

	<u> </u>	units quantities			
Quantity	Symbol	SI Units	Preferred Units	Imperial Units	Conversion
				_	from Imperial
					to SI multiply
					by:
length	L	m	m	ft	0.3048
mass	m	kg	kg	lbm	0.4536
time	S	S	S	sec	1
velocity	V	m/s	m/s	ft/sec	0.3048
angular velocity	ω	rad/s	rad/s	sec ⁻¹	1
force	F	Ν	kN	lbf	4.448
density	ρ	kg/m ³	kg/m ³	lbm/ft ³	16.02
specific volume	ν	m ³ /kg	m ³ /kg	ft ³ /lbm	0.06242
pressure	p	Pa	bar	lbf/ft ³	0.04788×10^{-3}
Energy	E (or U)	J	kJ	ft-lbf	1.356
Heat	Q	J	kJ	Btu	1055
Power	Ŵ	W	kW	ft-lbf/sec	1.356
specific enthalpy	h	J/kg	kJ/kg	Btu/lbm	2.326
specific entropy	S	J/kg K	kJ/kg K	Btu/lbm ⁰ R	4.187
Temperature	Т	K	K	⁰ R	5/9

Table. Units for some thermodynamics quantities.

Example Question: Express a pressure gauge reading of 50 psi in kilopascals.

Solution: 50
$$\left[\frac{lbf}{in^2}\right] \times 144 \left[\frac{in^2}{ft^2}\right] \times 0.04788 \left[\frac{kPa}{lbf/ft^2}\right] = 344.74 \, kPa$$
.

This is gauge pressure but to arrive at absolute pressure (predominantly used in thermodynamics) it is necessary to add atmospheric pressure ($\approx 100 \text{ kPa}$), which gives p = 444.74 kPa.

Example Question: Identify the extensive and intensive properties: (i) 100 m³ volume; (ii) 50 kJ kinetic energy; (iii) 70 kPa pressure; (iv) 100 MPa stress; (v) 50 kg mass; (vi) 10 m/s speed and finally; (vii) convert all extensive to specific properties given mass m = 50 kg.

Solution: (i) Extensive (if mass doubles, then so does V); (ii) Extensive (if mass doubles, then so does E); (iii) Intensive (pressure is independent of mass); (iv) Intensive (stress is independent of mass); (v) Extensive (mass doubles with mass doubling); (vi) Intensive (speed is independent of mass); (vii) specific

volume $v = \frac{V}{m} = \frac{100}{50} = 2m^3 / \text{kg}$; specific energy $\frac{E}{m} = \frac{50}{50} = 1 \text{ kJ} / \text{kg}$ and; specific mass $\frac{m}{m} = \frac{50}{50} = 1 \text{ kg} / \text{kg} = 1$.

Example Question: Express the following quantities in base SI units (kg, m, s, K): (i) Power; (ii) Kinetic Energy; (iii) specific entropy and (iv) specific weight.

Solution:

(i)
$$\begin{bmatrix} \dot{W} \end{bmatrix} = \llbracket Fv \rrbracket = \begin{bmatrix} N \times \frac{m}{s} \end{bmatrix} = \begin{bmatrix} \frac{kg m}{s^2} \times \frac{m}{s} \end{bmatrix} = \begin{bmatrix} \frac{kg m^2}{s^3} \end{bmatrix};$$

(ii) $\begin{bmatrix} E \end{bmatrix} = \begin{bmatrix} \frac{1}{2} mv^2 \end{bmatrix} = \begin{bmatrix} kg \times \left(\frac{m}{s}\right)^2 \end{bmatrix} = \begin{bmatrix} \frac{kg m^2}{s^2} \end{bmatrix};$
(iii) $\begin{bmatrix} s \end{bmatrix} = \begin{bmatrix} \frac{S}{m} \end{bmatrix} = \begin{bmatrix} \frac{J}{kg K} \end{bmatrix} = \begin{bmatrix} \frac{Nm}{kg K} \end{bmatrix} = \begin{bmatrix} \frac{kgm^2}{kg s^2 K} \end{bmatrix} = \begin{bmatrix} \frac{m^2}{s^2 K} \end{bmatrix};$
(iv) $\llbracket w \rrbracket = \begin{bmatrix} \frac{mg}{V} \end{bmatrix} = \llbracket \rho g \rrbracket = \begin{bmatrix} \frac{kg}{m^3} \times \frac{m}{s^2} \end{bmatrix} = \begin{bmatrix} \frac{kg}{m^2 s^2} \end{bmatrix}.$

Note: The 'specific weight' is the weight per unit volume of a material, hence showing that the term 'specific' does not always imply 'per unit mass'. Another example is the 'specific density' (specific gravity) which is defined as the ratio of the density of a substance (e.g. ρ_{oil}) to the density of a given reference material (usually ρ_{water}).

Definition of a State

The *state* of a system is a complete description of all the properties of the system, i.e. both the mechanical and thermodynamic properties. A *simple* system is defined by its volume, pressure, velocity and position.

A system is in the same state (e.g., after a series of processes) if and only if, *all the properties are identical* in both instances.

State point

The state of a system can be defined in a *state space*, which is depicted on a *state diagram*. The usual form of state diagram is two-dimensional, and each of the axes is an *independent* property. A *state point* is a point on the diagram representing the properties of the system at *any* instant. The state point is an *equilibrium* point.



A state point on a pressure-volume diagram

Change of state

When the state of a system alters, the change of state is defined by the two end states. In the figure the state changes from (p_1, V_1) to (p_2, V_2) .



Change of state from (p_1, V_1) to (p_2, V_2) .

Note that four paths are shown on the diagram, and any one of these is a possible route between the two states. It is not possible (yet) to define the route followed.

Important properties

Pressure p

Pressure is the force per unit area exerted by a system on its surface in the direction normal to that surface. Mathematically this can be defined as:

$$p = \lim_{\Delta A \to 0} \frac{\Delta F_n}{\Delta A}$$

where ΔF_n is the normal component of force acting on the small surface area $\,\Delta A$.

Pressure is a *continuum* concept, and it is supposed that the number of molecules per unit volume is large. This will usually be the case in mechanical engineering. However, in outer space the number of molecules per unit volume will be small, and then the concept of pressure is more difficult to define.

The units of pressure are Newton/square metre denoted by N/m^2 . This is sometimes referred to as the pascal (Pa). The pascal is an extremely small pressure, so usually multiples of pascals are used. Commonly used values are:

•	kilopascals (kPa)	$= 10^{3} Pa$
•	Megapascals (MPa)	$= 10^{6} \text{ Pa}$
•	bar	$= 10^{5} Pa$

The unit of pressure used in this course will be the *bar*, although different textbooks use different units. The bar is a convenient unit because a pressure of 1 bar is almost equal to standard atmospheric pressure [1 standard atmosphere = 1.013 bar = 1013 mbar]. Note that the atmospheric pressure quoted in meteorological forecasts is in millibars. It is recognised however that in the atmosphere, pressure varies with elevation; described in differential terms by the simple expression $dp = -\rho g dz$, where ρ is density (which depends on z) and g is acceleration (in free fall) due to gravity and p_0 is the pressure at ground level identified here by z = 0.

It is important to appreciate that in the vast majority of thermodynamic relationships absolute pressure is used, i.e.

 $p = p_{abs} = p_{gauge} + p_{atm}$

where p_{gauge} is gauge pressure (measured with a pressure gauge) and p_{atm} is atmospheric pressure (measured with a barometer). There are a number of devices for measuring pressure, which include:

- Manometers
- □ Gauges
- □ Electrical transducers

Density p

Density is a continuum concept and is defined as mass per unit volume:

$$\rho = \lim_{\Delta V \to 0} \frac{\Delta m}{\Delta V}$$

where Δm is the mass in the small region with volume ΔV . The units of density are kilograms per cubic metre denoted by kg/m³.

Specific volume v

Specific volume is the reciprocal of density and is defined as the volume per unit mass; i.e.

$$\nu = \lim_{\Delta V \to 0} \frac{\Delta V}{\Delta m} = \frac{1}{\rho}$$

The units of specific volume are cubic metres per kilogram, denoted by m³/kg.

Example Question: The mass of air in a room of dimensions $2.5 \times 4 \times 10$ m is estimated to be 123 kg. Determine the density and specific volume.

Solution:
$$V = 2.5 \times 4 \times 10 = 100 \text{ m}^3$$
, so $\rho = \frac{m}{V} = \frac{123}{100} = 1.23 \frac{\text{kg}}{\text{m}^3}$ and $v = \frac{1}{\rho} = \frac{1}{1.23} = 0.813 \frac{\text{m}^3}{\text{kg}}$

Example Question: The pressure in a bike tyre is recorded as 2100 mmHg gauge and the standard atmosphere is taken to be 760 mmHg. Mercury is some 13.6 times heavier than water and the density of water is 1000 kg/m³ and g = 9.81 m/s². Express both the absolute and gauge pressures in units of: kPa, bar and mmH₂0.

Solution: The relationship between pressure and height is $dp = -\rho g dz = \rho g dh$ with dh = -dz (h measured downwards), which gives the expression $p_{gauge} = \rho g h$.

$$p_{gauge} = \rho gh = 1000 \left[\frac{kg}{m^3} \right] \times 9.81 \left[\frac{m}{s^2} \right] \times 13.6 \times 2100 \times 10^{-3} [m] = 2.802 \times 10^5 \left[\frac{kg m}{s^2} \times \frac{1}{m^2} \right]$$
$$= 280.2 \times 10^3 \left[\frac{N}{m^2} \right] = 280.2 kPa = 2.802 bar$$
$$p_{atm} = \rho gh = 1000 \left[\frac{kg}{m^3} \right] \times 9.81 \left[\frac{m}{s^2} \right] \times 13.6 \times 760 \times 10^{-3} [m] = 1.014 \times 10^5 \left[\frac{kg m}{s^2} \times \frac{1}{m^2} \right]$$
$$= 101.4 \times 10^3 \left[\frac{N}{m^2} \right] = 101.4 kPa = 1.014 bar$$

Hence $p = p_{abs} = p_{gauge} + p_{atm} = 280.2 + 101.4 = 381.6 \text{kPa} = 3.816 \text{bar}$ In terms of mmH₂0: $p_{gauge} = 13.6 \times 2100 = 28560 \text{ mmH}_20$, $p_{atm} = 13.6 \times 760 = 10336 \text{ mmH}_20$, thus $p = p_{abs} = p_{gauge} + p_{atm} = 28560 + 10336 = 38896 \text{ mmH}_20$.

Temperature (t or T)

Temperature is a measure of molecular activity but since classical thermodynamics deals with macroscopic properties, molecular definitions are not that useful. Temperature is a property introduced by thermodynamics (the Zeroth law) and since temperature differences drive thermodynamic processes it is the most important property for the study of this subject. Temperature is a measure of how "hot" or "cold" a body is. However, in making that measurement it is important that the device used for measuring the temperature is in *thermal* (temperature) *equilibrium* with the body. Various (somewhat arbitrary) temperature scales have been established. Celsius [0 C] (formally called centigrade) and Fahrenheit [0 F] are related by

$$t_{\rm F} = \frac{9}{5}t_{\rm C} + 32 \ [^{0}\text{F}] \text{ or } t_{\rm C} = \frac{5}{9}(t_{\rm F} - 32) \ [^{0}\text{C}]$$

chosen to have 100 0 C (180 0 F) between the *ice (freezing) point* (0 0 C, 1.013 bar) and the *steam (boiling) point* (100 0 C, 1.013 bar) of water.

		Fahrenheit scale								
Q	20	³² 40	60	80	100	120	140	160	180	200 212
		Ó	10 20	30	40	50	60	70	80	90 100
ice + water + salt mixture		Fre	eezing poi f ice + wat mixture	int er	C	elsius	scale		Boiling of w	point ´ rater

Absolute (*continuous*) scales can be established with the help of the second law (more on this much later), Kelvin [K] and Rankine $[{}^{0}R]$ and take the form

$$T_{R} = t_{F} + 459.67 [^{0}R]$$
 and $T = t_{C} + 273.15 [K]$; it follows that $T = \frac{5}{9}T_{R}$,

where T = 0 K ($T_R = 0^0 R$) denotes *absolute zero*, where loosely speaking, all molecular activity stops.

The only way to obtain an accurate measurement of temperature (by a contact method) is when the measuring device and the system being measured are at the same temperature; this is referred to as being in *thermal equilibrium* (more on this later).

Example Question: The temperature of a body is 50 °F, so what is the temperature in °C, K and °R? Solution: $T_R = t_F + 459.67 = 50 + 459.67 = 509.67 \approx 510$ °R, $T = \frac{5}{9}T_R = \frac{5}{9} \times 509.67 = 283.15 \approx 283$ K and finally $t_C = T - 273.15 = 283.15 - 273.15 = 10$ °C.

Example Question: A gas containing pressure vessel with non-uniform wall temperature is suddenly isolated (i.e. mass and energy transfer is prevented). Is the system of gas contained in the pressure vessel in thermal equilibrium and if not why not?

Solution: Thermal equilibrium requires a uniform temperature throughout the volume of the system of gas. The non-uniform temperature of the walls of the pressure vessel suggests that this is not the case. In isolation and after a period of time it is expected that a uniform temperature is obtained and thermal equilibrium established. (The thermal behaviour described here is as a consequence of the 2^{nd} law but that comes much later in the course).

of

Definition of a Process

Path

If a system changes state slowly (compared to the reaction time of the system) it passes through a series of equilibrium states called a *path*. Such a path is shown in the figure below.

Process

The path through the succession of equilibrium points is called a *process*. The process in the figure is *defined by the two end states and the path.*



A change of state from state-point A to state-point B, passing through a series of *equilibrium* states.

Cycle

A cycle is a process whose end states are identical. The concept of a cycle is an **extremely** important one in thermodynamics, and many proofs are derived in thermodynamics by considering cyclic processes.



A cyclic change of state from state point A to state point B and back to state point A, passing through a series of equilibrium points.

Relationship between properties

The state of simple systems of constant mass and composition can be defined by two *independent* properties. Any other property can be evaluated from these two properties if the characteristics of the substance inside the system boundaries are known. Hence, **two independent properties are sufficient to define the state of simple systems of constant mass; the** *two property rule.*

<u>Thermal equilibrium</u>

Consider two systems, A and B, which are not at the same state, connected through a wall, as shown. This wall can be either a perfect insulator (*adiabatic* wall) or a perfect conductor (*diathermal* wall).



Two closed systems separated by a wall

The state of system A can be defined by any two properties (X, Y), while that of system B can be defined by (X', Y'). For the sake of clarity, let us assume that the state of system A is defined by its pressure p and volume V, while the state of system B is defined by pressure p' and volume V'. If the systems do not change state with time then the wall is an **adiabatic** one. If the systems *spontaneously* change state then the wall is a **diathermal** one.

Consider if systems A and B are not at the same state initially. If they are brought into contact with a **diathermal** wall then their states will spontaneously change until they ultimately reach a steady state: this steady state is called *thermal equilibrium*.

Zeroth law of thermodynamics

If three systems are brought into contact through a diathermal wall, then the following statement can be made after some time.

- A and C are in thermal equilibrium
- B and C are in thermal equilibrium

hence

• A and B are in thermal equilibrium, even though they are connected through an adiabatic wall.

This leads directly to the Zeroth law of thermodynamics

Two systems are in thermal equilibrium with each other if they are both in thermal equilibrium with a third system.

It is evident that system A and system B must have a common property which is given the name temperature. A system is in thermal equilibrium if and only if its temperature is uniform. Moreover, systems in thermal equilibrium with each other are said to be at the same temperature. A more detailed discussion on this can be found in Appendix I.



Measurement of temperature

The method of measuring temperature is to use a system (device) which has an observable property, and which can be maintained in thermal equilibrium with the system whose temperature it is required to measure. Such a measuring system will obey the Zeroth Law. Examples of devices for measuring temperature are given in Table 1.

Device type	Measurement
	property
Constant volume gas thermometer	pressure
Constant pressure gas thermometer	volume
Electrical resistance thermometer	resistance
Thermocouple	voltage
Liquid in glass thermometer	length

Table 1: Different devices for measuring temperature

In each of these devices for measuring temperature one property is maintained constant and another varies. By the two-property rule, if T = T(x, y), and if one property is kept constant, say x, then T = T(y), i.e. temperature is a function of y alone. If x and y were volume (V) and pressure (p) respectively, *Boyle's Law* is observed for different temperatures or different gases.

The method of use of a device for measuring temperature will be examined by considering a constant volume gas thermometer. A fixed volume of gas, indicated by the volume line, is contained in a vessel; this volume can be treated as a closed system. The vessel is immersed in the fluid whose temperature it is required to measure, and the volume of gas will change as the temperature changes: the gas obeys the perfect gas law pV = mRT. Thus T = pV/mR, and since m and R (the specific gas constant) are constant for this closed system, then T = T(p, V). If the volume is maintained constant, then T = T(p) and, in this case, $p\alpha T$. Hence, the temperature can be measured by evaluating the pressure required to bring the volume back to its initial value. A graph of ΔT against Δp will be a straight line.



Fig: Schematic diagram of constant volume gas thermometer

Temperature scales

There are two different scales of temperature:

• The thermodynamic scale of temperature which is independent of the thermometric substance, and is based on the Second Law of Thermodynamics; this will be introduced later in the course. This is a *continuous scale* of temperature.

• The International Temperature Scale (ITS-90). This has been defined by an international group of physicists meeting in 1990, and is based on establishing a number of fixed points on the temperature scales and interpolating between them. These are *discontinuous scales* of temperature used primarily for the purpose of equipment calibration.

The Celsius (or Centigrade) and Fahrenheit scales are the original ITS scales. These scales have been refined such that now the triple point of water (to be defined later) is given the temperature of 0.01°C, and the boiling point at a pressure of 1 atmosphere is 100°C. A number of other points are defined at lower and higher temperatures, and are defined in the Table below.

	Absolute Temperature (K)	Temperature (°C)
Triple point of equilibrium hydrogen	13.81	-259.34
Normal boiling point of equilibrium hydrogen	20.28	-252.87
Triple point of oxygen	54.36	-218.79
Normal boiling point of oxygen	90.19	-182.96
Triple point of water	273.16	0.01
Normal boiling point of water	373.15	100.00
Normal freezing point of zinc	692.73	419.58
Normal freezing point of silver	1235.08	961.93
Normal freezing point of gold	1337.58	1064.43

Table: Additional fixed points on International scale of temperature (just for information)

Example Question: A sealed pressurised canister contains gas at a gauge pressure of 1 bar at a temperature of 20 0 C and will fail when the gauge pressure reaches 5 bar. Assuming an ideal gas (i.e. one satisfying pV = mRT) and that $p_{atm} = 1$ bar, determine the temperature at which the canister fails. It can be assumed that the failure mechanism is independent of temperature and that the canister's internal volume hardly changes.

Solution: Please take note that the gas law involves absolute pressure and temperature and for this case $\frac{p}{T} = \frac{mR}{V} = \text{constant.}$ It follows that

$$\frac{\mathbf{p}_1}{\mathbf{T}_1} = \frac{\mathbf{p}_2}{\mathbf{T}_2} \Longrightarrow \mathbf{T}_2 = \mathbf{T}_1 \frac{\mathbf{p}_2}{\mathbf{p}_1} = (20 + 273) \frac{5+1}{1+1} = 293 \times \frac{6}{2} = 879 \,\mathrm{K} = 606^{\,\mathrm{o}}\mathrm{C}$$

A Note on SI Units (for information only)

Four of the seven SI base units are to be redefined in terms of fundamental constants.

(i) The second (s) remains unchanged tied to the radioactive decay of the caesium-133 atom.

- (ii) The metre (m) remains unchanged tied to the speed of light in a vacuum.
- (iii) The candela (cd) which is a measure of luminous intensity remains unchanged.
- (iv) The kilogram (kg) will in future be tied to the Planck constant $h = 6.63 \times 10^{-34}$ Js.
- (v) The Kelvin (K) will in future be tied to the Boltzmann constant $k = 1.38 \times 10^{-23} \text{ J/K}$.
- (vi) The Ampere (A) will in future be tied to the charge of the proton, i.e. $+1e \sim 1.6 \times 10^{-19} C$.
- (vii) The Mole (mol) will in future be tied to the Avogadro constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$.

APPENDIX: Temperature

In the derivation that follows the concept of temperature is derived via the Zeroth law. In order to do this, three systems 'A', 'B' and 'C' are utilised. For the sake of clarity let us assume that the states of systems 'A' and 'B' are defined in terms of pressure and volume (hence the cylinder/piston arrangement). It is important to realise that using pressure and volume as our reference properties is entirely irrelevant to the discussion, and that **any** two thermodynamic properties would suffice.

Consider the system shown overleaf



As the piston in system 'A' moves up and down, the pressure and volume change. This change is marked on the sketch as the locus of points. We imagine that for the whole duration of piston 'A's movement, the system is in thermal equilibrium with system 'C' via the diathermal wall. This implies that if movement of the piston ceases, then the conditions inside system 'A' will not change spontaneously. The locus of states passed through by system 'A' under the restriction that it is in thermal equilibrium with system 'C' is referred to as an *isotherm*.

Similarly, we assume that the piston in system 'B' also moves up and down, changing its pressure and volume as it does so. We note that neither p" nor V" in system 'B' need bear any relation to that in 'A'. During piston 'B's motion, we again assume that the fluid it compresses is in thermal equilibrium with system 'C'. Again, the locus of points followed by system 'B' is shown on the right hand side of the above sketches, while the system 'C' state point is also shown.

Now, if system 'A' is in thermal equilibrium at all times with system 'C', and system 'B' is in thermal equilibrium at all times with system 'C', then it follows from the zeroth law that system 'A' must be in thermal equilibrium with system 'B'. This is despite the fact that systems 'A' and 'B' cannot communicate because of the adiabatic wall. All these systems are in *thermal equilibrium* with each other, and must share a common property. We say that they are at the same **temperature**.

Systems in thermal equilibrium with each other are said to be at the same temperature.

Tutorial Questions

- 1. Draw a schematic diagram of a gas turbine used for the generation of electrical power. Show where the fuel is admitted and the work output is obtained.
- 2. Draw a schematic diagram of an aircraft gas turbine, and show where the fuel is admitted and how the work output is achieved.
- 3. Show schematically how the fuel is used in a petrol (spark ignition) engine to produce power output.
- 4. Figure 1 shows a bottle which is initially empty (contains a vacuum). It is then filled with water from a jug. Show the system boundaries that enable the process involved to be considered as
 - (i) an open system;(ii) a closed system.



Fig 1: Filling a bottle from a jug

- 5. Define the following properties and give two examples
 - (i) intensive;
 - (ii) extensive;
 - (iii) specific.
- 6. The term $V^2/2$ is a(n) property of a system: it represents energy.
- 7. If you climb a mountain which of the following parameters would be properties of your journey?
 - (i) distance;
 - (ii) geographical location (latitude and longitude);
 - (iii) height;
 - (iv) time taken.
- 8. Which of the following pressures is the largest?

(i) 10^5 millibars	(ii) 3×10 ⁶ Pa
(iii) 105 bar	(iv) 30 MPa
(iv) 3×10^6 N/m ²	

CHAPTER 2

WORK AND HEAT

THE CHAPTER COVERS:

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Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 2 "Energy, Energy Transfer and General Energy Analysis" pages 70-77 and Chapter 4 "Energy Analysis of Closed Systems" pages 163-169.

Introduction

Understanding the first law of thermodynamics requires some familiarisation with two quantities of energy transfer across the boundary of a system: work and heat. Work is considered in some detail but heat is covered in somewhat broader terms since detailed analysis is beyond the scope of a first level module (examined further in the third year). The first law is often considered to be relatively benign (i.e. easy to understand) by students being an extension of the *law of conservation of energy*, which infers that energy can neither be created nor destroyed, i.e. whatever energy was present at the start of the universe remains the same and will remain invariant until its end. However, thermodynamics is a subtle subject and like the zeroth law (which inferred the existence of the property temperature) the first law infers the existence of a property (termed energy); there is no requirement for us to assume *a priori* that the property energy exists. It transpires that energy is a property of a system yet work and heat are not. Is this obvious? How can it be shown? How do we quantify work and heat if they are not properties?

Both work and heat are described by their interaction between the system and its surroundings. For a closed system the flow of energy between a system and its surroundings principally takes only one of two forms and these forms are work and heat. But if it is true that work and heat are merely forms of energy transfer, then what distinguishes them?

Work is motion against an opposing force and in mechanical terms is the product of force times the distance moved in the direction of the force. In thermodynamic terms however all types of work can be shown to be equivalent to raising a weight in a gravitational field. Heat on the other hand is energy transfer resulting from a temperature difference. Prior to examining these issues in detail it is prudent at this point to introduce the first law, which for a closed system in mathematical terms is:

 $dU = \delta Q - \delta W$ (or $dU = \delta Q + \delta W$) depending on the sign convention used for positive work.

The first law relates an increment in energy dU (a property) to increments in heat δQ and work δW which are not properties (the notation reflects this). Surprising as it appears the expression $\delta Q - \delta W$ is a property despite δQ and δW not being so.

Moreover, the notation used here (i.e. d and δ) requires some explanation but note that (for a *non-quasi-static* process, i.e. a real process involving time) $dU = \dot{U}dt$, $\delta Q = \dot{Q}dt$ and $\delta W = \dot{W}dt$ with dt an increment of time and $\dot{U} = \frac{dU}{dt}$ but it WOULD NOT BE CORRECT to replace the heat and work rates \dot{Q} and \dot{W} with derivatives $\frac{dQ}{dt}$ and $\frac{dW}{dt}$, respectively; the use of the symbols d and δ reflects this. It is appreciated however that these nuances require further explanation but are introduced here merely to illustrate that the first law is not as obvious as it first appears.

Thermodynamic definition of Work

Work is done **by** a system when the sole effect on everything external to a system (the surroundings) would be the raising of a weight.

This definition reinforces the idea that work is essentially about energy transfer since the potential energy (height of the weight) of the surroundings is increased by the system. Energy in this context is nothing more than the capacity to do work and work is something we know about from simple mechanics.

Examples



As the battery discharges through motor the weight is lifted and consequently the work done **by** the system is positive. If the weight is allowed to fall (and thereby drive the motor), the motor would act as a generator and recharge the battery. Work would be done **on** the system is positive.



To get the block to move and overcome friction, the weight drops. The surroundings is losing (potential) energy and consequently the system must be gaining energy by the same amount (assuming no other types of loss).

Energy entering the system in this manner is defined as negative work done **by** the system or positive work done **on** the system.

Similarly (possibly confusingly) work done by the surroundings is positive but on the surroundings it is negative.

In order to stir the fluid, the weight must drop and work is done <u>on</u> the system is positive. Work done by the system on the surroundings is negative. Alternatively, one could say that the work done on the system by the surroundings is positive. This system is dissipating energy (via fluid friction). It cannot be reversed. What do you think will happen to the fluid?



Consider two cases:

1. As the pressure in the bag increases, the bag expands, pushing on the connecting rod and lifting the weight. In this case work done by the system is positive.

2. If the pressure reduces, the bag shrinks, the weight lowers and work done by the system is negative.

Quasi-Static Processes

The thermodynamics of principal concern in this course is essentially **equilibrium** thermodynamics. Equilibrium in this case means that, in the absence of external stimuli, the thermodynamic state of the system *will not* change *spontaneously*.

Quasi-static change in a system is change that takes place whilst maintaining equilibrium. On a practical level such changes take place very slowly.

The concept of equilibrium can be demonstrated by analogy to mechanical systems.



System

Mechanical equilibrium: in the absence of external stimuli, the ball will remain stationary (external = from outside the system).

Not in **mechanical equilibrium**; even in the absence of external stimuli, the state of the system (i.e. the position of the ball) changes spontaneously.

By comparison,



Not in **thermodynamic equilibrium**; in absence of external stimulus, pressure waves bounce backwards and forwards

 $\Rightarrow p = p(\mathbf{x}, t) \neq \text{const}$

$$T = T(\mathbf{x}, t) \neq \text{const}$$

Pressure and temperature are defined locally in this case.

Thermodynamic equilibrium; in the absence of external influences (heat and work transfers) the thermodynamic state is stationary (p & T etc. are constant).



The Effect of Work on the Surroundings

It has been shown that work is a kind of energy transfer. Energy can neither be created nor destroyed, merely transferred.

To reiterate,

- If work is done <u>by</u> a system, it is done <u>on</u> the surroundings. If $W_{sys} > 0$ then $W_{surr} < 0$ and $W_{sys} + W_{surr} = 0$
- If work is done <u>on</u> a system, it is done <u>by</u> the surroundings. If $W_{svs} < 0$ then $W_{surr} > 0$ and $W_{svs} + W_{surr} = 0$

where W_{svs} and W_{surr} represent the work done by the system and surroundings, respectively.

Representation of Work



The sign convention shown in this sketch is arbitrary. Many texts (for example Rogers and Mayhew) use the opposite sign convention for work. The actual convention used is unimportant, *so long as you are consistent*.

Choosing the Rogers and Mayhew sign convention means making sure that all positive work terms in your equations become negative and vice versa.

Example Question: The force needed to slowly compress a nonlinear spring (the system) is given by the expression $F = 200u + 40u^3 [N]$, where u is the displacement of the spring from its original length measured in metres. Determine the work done **by** and **on** the system along with work done **by** and **on** the surroundings in compressing the spring by 0.6 m.

Solution: It is observed that energy is being transferred from the surroundings to the spring which increases its potential energy (i.e. its capacity to do work). Thus it must be that case that work done by the system is negative, i.e. $W_{sys} < 0$ and work done by the surroundings is positive, i.e. $W_{surr} > 0$. Simply reverse the signs to obtain for work done on the system and surroundings.

The increment of work done by the system is $\delta W_{svs} = -Fdu$ and it follows that

$$W_{sys} = \int \delta W_{sys} = -\int_{0}^{0.6} F du = -\int_{0}^{0.6} (200u + 40u^{3}) du = -(100u^{2} + 10u^{4}) \Big|_{0}^{0.6}$$
$$= -(100 \times 0.6^{2} + 10 \times 0.6^{4}) = -37.3J$$

Note that $W_{surr} = 37.3 \text{ J}$ and $W_{sys} + W_{surr} = 0$, i.e. energy has been conserved (it has merely moved from the surroundings to the spring).

Different types of work

'Mechanical' work

'Mechanical' work is the type of work covered in A-level and introductory mechanics modules.

$$\delta W_m = \mathbf{F} \bullet \mathbf{du} = (F_1 \mathbf{i} + F_2 \mathbf{j} + F_3 \mathbf{k}) \bullet (du \mathbf{i} + dv \mathbf{j} + dw \mathbf{k}) = F_1 du + F_2 dv + F_3 dw = |\mathbf{F}| |\mathbf{du}| \cos \theta$$

where θ is the angle between the vectors **F** and **du**.

Displacement work

In thermodynamic systems, one of the most common types of work is **displacement** work. Consider a constant internal pressure p acting on the surface of a control volume and consider further the control volume expanding slightly by the amount dV. Work is being done by the system on the surroundings.



Contribution to the total force \mathbf{F} from pressure *p* acting on area *dA* is

 $d\mathbf{F} = p \, d\mathbf{A} = p \, \mathbf{n} dA$ (**n** is an outward pointing unit normal and is in the direction of the force $d\mathbf{F}$)

Contribution to the increment in work done $\delta W_{\mathbf{D}}$ (denoted here δW_{dA}) from pressure *p* acting on area *dA* where boundary is displaced by **du** is

 $\delta W_{dA} = \mathbf{dF} \bullet \mathbf{du} = p\mathbf{n} \bullet \mathbf{du} dA = p dV_{dA}$, where from the geometry $dV_{dA} = \mathbf{n} \bullet \mathbf{du} dA$

Note that the volume increment dV_{dA} refers to a change in volume resulting from an increment of displacement **du**.

The total increment in work done δW_D is obtained on summation (integration), i.e.

$$\delta W_D = \int \delta W_{dA} = \int p dV_{dA} = p \int dV_{dA} = p dV$$



This (i.e. $\delta W_D = p dV$) is one of the most important equations you will use in first-year thermodynamics.

For the piston depicted with cross sectional area A moving an incremental displacement du; the formula gives

$$\delta W_{\rm D} = pdV = pAdu$$

Example Question: Air is compressed by the action of a piston in a cylinder such that the volume changes from 10 to 1 m³. The initial pressure is 1 bar. Assume the process is performed quasi-statically and isothermally and that the air behaves as an ideal gas (i.e. it satisfies pV = mRT). Determine the work done by the system (the air). Comment also on the work done by the surroundings and the work done on the piston, i.e. by any force applied to the piston to compress the air.

Solution: The critical formula is $\delta W_D = pdV$ but note that $pV = mRT = p_1V_1$ (since isothermal).

$$W_{1-2} = \int \delta W_{D} = \int_{V_{1}}^{V_{2}} p dV = P_{1} V_{1} \int_{V_{1}}^{V_{2}} \frac{dV}{V} = P_{1} V_{1} \ln V \Big|_{V_{1}}^{V_{2}} = P_{1} V_{1} \ln \left(\frac{V_{2}}{V_{1}}\right) = (1 \times 10^{2}) \times 10 \times \ln\left(\frac{1}{10}\right) = -2302.6 \text{kJ}$$

The work done by the system is evidently negative and hence the work done by the surroundings is positive. The work done by the surroundings is also 2302.6kJ. Note here, that the surroundings include the piston. The work arising as consequence of any force applied to the piston in the surroundings is likely to be greater than 2302.6kJ as a consequence of possible losses may have occurred as a consequence of friction at the piston walls.

Example Question: During a particular process, a spherical balloon is inflated from a radius of 0.1m to a radius of 0.2m. During this time, the pressure is found to satisfy $p \propto r^{3/4}$, where r is the radius of the balloon. The volume of the sphere is given by the formula $V_{sphere} = (4/3)\pi r^3$.

(i) Show that the displacement work by the system of gas during the process can be written as

$$W_{1-2} = 4\pi \int_{r}^{r_2} r^2 p dr$$

where p is a function of radius.

- (ii) Derive an equation for the work done on the balloon by the gas during this process.
- (iii) If the constant of proportionality between pressure and radius is $k = 562 \times 10^3 \text{ N/m}^{11/4}$, calculate the total work done on the balloon.

Solution:

(i) The critical formula is $\delta W_D = pdV$ and since $V = \frac{4}{3}\pi r^3$ it follows that $dV = 4\pi r^2 dr$ hence $\delta W_D = pdV = 4\pi r^2 pdr$ and the result $W_{1-2} = 4\pi \int_{-2}^{r_2} r^2 pdr$ immediately follows.

(ii) Since
$$p \propto r^{3/4}$$
 it follows that $p = kr^{3/4}$ for some constant k, where

$$\begin{bmatrix} p \end{bmatrix} = \begin{bmatrix} \frac{N}{m^2} \end{bmatrix} = \begin{bmatrix} kr^{3/4} \end{bmatrix} = \begin{bmatrix} k \end{bmatrix} \begin{bmatrix} m^{3/4} \end{bmatrix} \Rightarrow \begin{bmatrix} k \end{bmatrix} = \begin{bmatrix} \frac{N}{m^2 m^{3/4}} \end{bmatrix} = \begin{bmatrix} \frac{N}{m^{11/4}} \end{bmatrix}$$

Therefore $W_{1-2} = 4\pi \int_{r_1}^{r_2} r^2 p dr = 4\pi k \int_{r_1}^{r_2} r^{11/4} dr = \frac{16\pi k}{15} r^{15/4} \Big|_{r_1}^{r_2} = \frac{16\pi k}{15} (r_2^{15/4} - r_1^{15/4})$
(iii) Assuming $k = 562 \times 10^3 N / m^{11/4}$ it follows that

$$W_{1-2} = \frac{16\pi k}{15} (r_2^{15/4} - r_1^{15/4}) = \frac{16\pi 562 \times 10^{-3}}{15} (0.2^{15/4} - 0.1^{15/4}) = 4.171 \text{kJ}$$

Work done in Creating a Surface



Consider a soap film in the frame shown. Let the frame be L wide and the wire CD move a distance du. The force exerted by the soap film in the wire *CD* is $F = 2\Gamma L$.

where Γ is surface tension and L is the length of the wire. Note that F resists expansion and the factor 2 comes from there being a front and a back to the film.

Therefore, the work done by the system is: $\delta W_{S} = -F \, du = -2\Gamma L du = -\Gamma dA,$ where dA is the surface area created.

Shaft Work Consider a shaft running in a turbine.



A shear stress is imposed on the shaft by the blades which are, in turn, driven by the flow over them.

The incremental displacement at radius r is $du = rd\theta$, where $d\theta$ is an increment of rotation of the shaft.

The force acting at radius r on area dA is $dF = \tau dA$, where τ is the shear stress acting on dA in a tangential direction.

The increment in work done due to dF and du is

$$\delta W_{dA} = \tau r d\theta dA = dF \, du = dF \, r d\theta = dT d\theta$$

where dT is a contribution to torque T. The total increment in shaft work done δW_s is obtained on summation (integration), i.e.

$$\delta W_{s} = \int \delta W_{dA} = \int_{A} \tau r d\theta dA = d\theta \int_{A} \tau r dA = d\theta \int dT = T d\theta$$

dF

where T is the torque acting to the shaft.

Example Question: The drive shaft in a motor car delivers a constant 100 Nm torque as it rotates 1000 revolutions. Calculate the work done delivered by the shaft.

Solution: The important formula is $\delta W_s = T d\theta$, which integrates to give

$$W_{1-2} = \int \delta W_{s} = \int_{\theta_{1}}^{\theta_{2}} T d\theta = T \theta \Big|_{\theta_{1}}^{\theta_{2}} = T(\theta_{2} - \theta_{1}) = 100 \times 2\pi (1000 - 0) = 628.32 \text{ kJ}$$

An Observation (incremental work terms look alike)

In the examples just cited, the infinitesimal work done by a system has had the form

$$\delta W = F_k dX_k$$

where in the literature, F_k is referred to as a generalised force and dX_k is called a generalised displacement.

System	Generalised force	Generalised displacement	Work
Mechanical (linear)	F (force)	du	F∙du
Mechanical (rotational)	T (torque)	dθ	Τdθ
Mechanical (displacement)	p (pressure)	dV	pdV
Mechanical (stretching)	au (tension)	$\mathbf{d}\ell$	$ au{ m d}\ell$
Physico-chemical (surface tension)	Γ (surface tension)	dA	$-\Gamma dA$
Electrical	V (voltage)	dQ _e	-VdQ _e

Polytropic Processes

Polytropic processes capture many practical thermodynamic compression/expansion processes that satisfy the relationship

 $pV^n = \text{constant} \qquad 0 \le n < \infty$.

or equivalently $pv^n = \text{constant}$, which obtained on dividing through by m^n for mass m.

The constant *n* is called the *polytropic index of expansion* or *compression* (or simply *polytropic index*)



Processes 1-2, 1-4 and 1-5 are **expansions** (because the volume increases) whilst processes 2-1, 4-1 and 5-1 would be **compressions**.

- Process 1-3 takes place at constant volume. (isochoric)
- Process 1-2 takes place at constant pressure. (isobaric)
- If pV = mRT (or pv = RT), then process 1-4 takes place at constant temperature. (isothermal)
- If $n = \gamma$, where γ is the ratio of specific heats (adiabatic index), then process 1-5 for this particular value of n takes place at constant entropy (much more on this much later) (isentropic)

Evaluating the displacement work done in a polytropic process

Recall that (mechanical) displacement work is $\delta_W = pdv$. (obtained from $\delta W = pdV$ on dividing by *m*) Consider a process described by $pv^n = \text{const}$. This can be seen in the sketch below



Going from 1-2 with *v* increasing gives dv > 0. Now p > 0 therefore

$$\delta w = p \mathrm{d} v > 0$$

The area under a *p*-*v* curve is evidently of significance.

Set $pv^n = C$ and observe that

 $\delta w = \frac{C}{v^n} dv = Cv^{-n} dv = \frac{C}{1-n} dv^{1-n}$ (this last step requires $n \neq 1$)

The **elemental** work done δw in the shaded region and total work done in going from $1 \sim 2$ is obtained on summation (integration) to give

$$w_{1-2} = \int_{1}^{2} \delta w = \int_{v_{1}}^{v_{2}} p dv = \int_{v_{1}}^{v_{2}} Cv^{-n} dv = \frac{C}{1-n} \int dv^{1-n} = \left[\frac{Cv^{1-n}}{1-n}\right]_{v_{1}}^{v_{2}}$$

Set $p_1v_1^n = C = p_2v_2^n$ and it follows that

$$w_{1-2} = \frac{p_2 v_2^{n} v_2^{1-n}}{1-n} - \frac{p_1 v_1^{n} v_1^{1-n}}{1-n}$$
$$= \frac{p_2 v_2 - p_1 v_1}{1-n}$$

If n = 1, then $p = \frac{C}{v}$ and $C = p_1 v_1 = p_2 v_2$, so it follows that

$$w_{1-2} = \int_{v_1}^{v_2} C \frac{dv}{v} = C \ln\left(\frac{v_2}{v_1}\right) = p_1 v_1 \ln\left(\frac{v_2}{v_1}\right) = p_2 v_2 \ln\left(\frac{v_2}{v_1}\right)$$

Example Question: During a particular process, a spherical balloon inflates (quasi-statically) from a radius of 0.1m to a radius of 0.2m. During the inflation process the pressure behaves polytropically (i.e. $pV^n = C$) with a polytropic index $n = -\frac{1}{3}$. The volume of the sphere is given by the formula $V_{\text{sphere}} = (4/3)\pi r^3$, where r is the radius of the balloon and the initial pressure in the balloon is 1 bar. Assuming the inflation process is resisted determine the work done by the system (the gas) on the balloon.

Solution: The formula $W_{1-2} = \frac{p_2 V_2 - p_1 V_1}{1 - n}$ is applicable here, where $V_1 = (4/3)\pi r_1^3$, $V_2 = (4/3)\pi r_2^3$ and $p_2 = p_1 \left(\frac{V_1}{V_2}\right)^{-\frac{1}{3}} = p_1 \left(\frac{r_2}{r_1}\right) = 1 \times \left(\frac{0.2}{0.1}\right) = 2$ bar. Substitution gives $W_{1-2} = \frac{p_2 V_2 - p_1 V_1}{1 - n} = \frac{4}{3}\pi \frac{p_2 r_2^3 - p_1 r_1^3}{1 - (-\frac{1}{3})} = \pi (p_2 r_2^3 - p_1 r_1^3) = \pi (2 \times 0.2^3 - 1 \times 0.1^3) \times 100 = 4.7$ kJ

Is Work a Property?

Consider the following example to demonstrate (again) how work is not a property. Consider a system which moves between two state points 1 and 2. These state points are defined in terms of two properties. For definiteness, the properties of pressure and total volume are used here.



Consider the work done by the system

- By moving along path I
- By moving via state point a, along paths II and III

The work done by moving along path I is $W_{1-2} = \int_{1-I-2} p \, dV = \frac{p_1 V_1 - p_2 V_2}{n-1}$. The work done moving along paths II and III is $\widetilde{W}_{1-2} = \int_{1-II-a} p \, dV + \int_{a-III-2} p \, dV$.

Now, along path II, the volume is constant and dv=0 (isochoric process), hence $\int_{1-U-a} p \, dV = 0$.

Along path III, p=constant, and $\int_{a-III-2} p \, dV = p_2(V_2 - V_a) = p_2(V_2 - V_1)$ $p_2V_2 - p_2V_3$

In general $\frac{p_2V_2 - p_1V_1}{1 - n} \neq p_2(V_2 - V_1)$, so it follows that $W_{1-2} \neq \widetilde{W}_{1-2}$.

i.e. the work transfers are different in general. Given that the end points are the same in each process, but the work transfers differ, it can be concluded that work cannot be a property.

Note that since work done is area under a p-v curve it can come as no surprise that $W_{1-2} \neq \widetilde{W}_{1-2}$; apparent on simple inspection of the figure above.

Heat

Work was a form of energy transfer which is illustrated in an example where a weight is lifted by the action of a piston.



As the fluid in the cylinder expands, the system **does** work on the surroundings (in this case, the linkage/weight mechanism). The work done **by** the system causes a potential energy increase in the weight – energy has been transferred **to** the surroundings).

In a similar vein, heat is a form of energy that is transferred from one body to another. Heat is transferred by virtue of a **temperature difference**. Heat as a mode of transferring energy, is intrinsically different to work as a mode of energy transfer. The difference stems from the Second Law of Thermodynamics examined later in the course.

In thermodynamics, processes can be brought about both by temperature differences and forces. This is in contrast to mechanics, in which forces alone govern processes.

In a previous section on Work the concept of a **quasi-static** process was considered. In order to approximate **quasi-static** processes in thermodynamic systems it is necessary that the processes undertaken are infinitely slow (to remove the influence of transients such as pressure waves). The same conditions must hold for heat transfer. The systems considered in 1st year thermodynamics are on the whole limited to systems with a single, well defined **temperature**.

In the kind of thermodynamics considered here the **mode** of heat transfer is often unimportant but some information on this is provided in the Appendix I.

In summary:

Heat (transfer) is the interaction between systems which occurs by virtue of temperature differences.

- 1. Heat interactions are associated with energy transfers
- 2. Heat interactions are transitory phenomena.
- 3. Heat is energy **transmitted** across a boundary.
- 4. Heat is NOT a quantity of energy contained in a system.
- 5. If two points at different temperatures are brought into contact, then heat is the energy transferred; the process ceases when the temperatures are equal (Zeroth Law).
- 6. Heat is not a property. (see Appendix II)

Demonstration of point 4.

• A similar demonstration led Count Rumford (between 1787-1799) to conclude that heat (or in his time, 'Caloric') was not an indestructible fluid contained within a body.

The correct physical phenomena in this demonstration are:

- Friction existing between the duster and desktop
- Work being **done** on the duster by moving it back and forth
- Work converted to heat by friction.

The incorrect ideas circulating prior to the work of Count Rumford were that bodies were filled with a mysterious fluid called caloric. This fluid was liberated by movement, and as it leaked out, it led to



the body being perceived as warm. In the duster example just quoted, however, we have a simple refutation of the caloric theory. The process can continue practically indefinitely, but if heat were contained in the body as caloric, then surely it would run out? That is the amount of caloric contained in the body would be a finite resource.

Sign Convention and Units

In this course, the following sign conventions are adopted.

- Heat into a body is positive;
- Heat out of a body is negative

which are opposite to those adopted for Work. As with work, *total* and a *specific* heat transfer can be defined. The capital letter Q is reserved for total heat transfer, and use a lower case q for the specific heat

transfer, i.e. $q = \frac{Q}{m}$, where q is the heat transfer associated with 1kg of working fluid.

The standard SI unit of heat is the **Joule** and remember that 1J = 1Nm. This emphasises the similarity between heat and work.

Example Question: (making use of the first law for closed systems)

A system, comprising a cylinder enclosed by a piston, is maintained at a constant pressure of 5 bar while 12.5 kJ of heat is transferred to the cylinder. If the internal energy of the system is unchanged during the process, find the change in the system volume as a result of the heat transfer.



Solution: From the first law of thermodynamics $Q_{1-2} - W_{1-2} = E_2 - E_1 = 0$ (here), so it follows that
$$Q_{1-2} = W_{1-2} = \int_{1}^{2} p dV = p \int_{1}^{2} dV = p(V_2 - V_1) = p \Delta V$$
.

Putting the numbers in (watch for inconsistent units)

$$\Delta V = \frac{Q_{1-2}}{p} = \frac{12.5 \times 10^3}{5 \times 10^5} = 0.025 \text{m}^3$$

An Appreciation of Magnitudes

It is useful to have an appreciation of the 'size' of a Joule in relation to tangible, everyday devices. To that end, note:

- 1. 1Cal = 4.1868 J (Cal = Calories)
- 2. 1 Calorie is the amount of energy required to raise the temperature of 1 gram of water by 1°C, when that water is initially at 15°C.

or, preferably

2b. 1 kilocalorie (kcal) is the amount of energy required to raise the temperature of 1 kg of water by 1°C, when the water is initially at 15°C.

The figures below give some indication of the energy and the power (energy per unit time) associated with some common processes.



Heat Processes on State Diagrams

As discussed previously (under the restriction of quasi-static processes) any *two* thermodynamic state variables can be used as axes to sketch the process. The same is true of heat transfer. Provided the heat transfer takes place infinitely slowly (to avoid temperature gradients), the system will have well defined, single values for pressure, temperature etc. Consequently, it is possible to draw the process on a state diagram.



Recall our earlier example of the bike pump in Appendix II. Either work or heat transfer can be used to move the thermodynamic state of the system from an initial point to a final point. It follows that it should be possible to devise a method by which the system is moved from state point 1 to state point 2 by (say) a heat transfer, and returned by (say) a work transfer back to state point 1. These processes can be drawn on the state diagram as



Once one accepts that it is possible to represent both heat and work processes on the same diagram, we can think up different combinations of heat and work which will move the system between states 1 and 2.



In both cases shown in the previous two sketches, the system ends at the same state point from which it starts. The process 1-2-1 shown in the sketches is referred to as a **cyclic process**. Cycles are of central importance in relating heat and work transfer. The manner in which we relate heat and work transfer is via **the First Law of Thermodynamics**.

APPENDIX I: Modes of Heat Transfer (for information only)

In the kind of thermodynamics consider here the **mode** of heat transfer is often unimportant. For example, in order to calculate the thermal efficiency of a power station, it is not necessary to know that turbulent convection is responsible for enhanced heat transfer in the boiler. It is nevertheless often helpful when trying to understand **what heat is** to examine the modes by which heat transfer takes place.

There are three modes of heat transfer:

- Conduction;
- Convection;
- Radiation.

Conduction

Conduction can take place in both fluids and solids. In solids, thermal energy is transmitted by vibrations of the atoms about their mean position, and by internal radiation.

The heat flux \dot{q} through a solid, is the **rate** at which thermal energy is transmitted and can be related to the temperature gradient using *Fourier's Law* of heat conduction, which in one-dimensional problems can be written as

$$\dot{q} = -\lambda \frac{dT}{dx}$$
.

The negative sign indicates that the heat flow is **down** the temperature gradient.

Example Question:

Calculate the heat flux through $1m^2$ of a household wall on a cold and stormy night. Assume that outside, it is 0°C and inside it is 20°C. Assume also that the wall consists of a single layer of bricks, 100 mm thick, with a constant thermal conductivity $\lambda = 0.5$ W/mK.

Solution: Fourier law $\dot{q} = -\lambda \frac{dT}{dx}$ can be applied in differential form, i.e. $\dot{q} dx = -\lambda dT$, which can be

integrated to give $\dot{q}(x_1 - t_1) = -\lambda(T_2 - T_1)$ or equivalently $\dot{q} = -\lambda \frac{\Delta T}{\Delta x}$.

Here ΔT is the temperature difference between the inside and the outside of the wall, and Δx is the wall thickness. Putting in the numbers gives

$$\dot{q} = -\frac{0.5}{(0-100) \times 10^{-3}} = -100 \frac{W}{m^2}$$

In metals, the conduction process is further enhanced by the additional redistribution of energy arising from the large number of electrons drifting through the material. This explains why good electrical conductors are usually also good thermal conductors.

Conduction is also found in fluids. Unlike solids, fluids do not have a regular lattice structure. Rather, atoms are allowed to move about more or less at random. The average spacing between atoms in a fluid is much larger than in a solid. This large degree of molecular spacing, coupled with their random motion means that the molecules in fluids have a large **mean free path**. The mean free path is the average distance a particle can move before being influenced by another particle. Consequently, it takes longer for thermal energy to be transmitted between particles and hence, thermal conductivity in fluids is usually lower than that of a solid.

Convection

This mode of heat transfer occurs exclusively in fluids. We can identify two types of convective heat transfer; natural and forced.

Natural Convection

Imagine a heated surface, mounted horizontally, and above which is a fluid.



The layer immediately adjacent to the hot surface is heated by conduction. As the fluid elements heat up, their density diminishes, and buoyancy forces lift them up away from the surface. Cool fluid replaces the hot fluid as it rises, and the process begins again.

Natural convection is responsible for heating in rooms and the onshore breezes found in the afternoon in hot parts of the world.



Forced Convection

In most engineering applications, forced convection is the prevalent mode of convective heat transfer. Like the natural convection case, fluid close to a hot surface is initially heated by conduction.



Industrial flows are usually **turbulent.** For the purpose of our discussion turbulence can be thought of as consisting of a large number of vortices of differing sizes. The practical consequence for us is that turbulence introduces **mixing** – hot elements are mixed out away from the surface, and cool elements are mixed in; thus

heat is again transferred from the surface.

In convective heat transfer, exact analytic expressions for the heat transfer rate are seldom available. For engineering calculations heat flux is approximated by

 $\dot{q} = h(T_B, T_B)$

where h is an heat transfer coefficient, T_s is surface temperature and T_b is bulk fluid temperature.

Radiation

This mode of heat transfer is electromagnetic in origin, and requires no medium through which to pass. For most engineering processes, radiation plays a relatively minor part. At this stage, it suffices to say that the radiative heat flux \dot{q} can be approximated using

$$\dot{q} = \varepsilon \sigma (T_{\mathbf{m}}^{\mathbf{m}} - T_{c}^{4})$$

where ε is the emissivity (a number between 0 and 1 where $\varepsilon = 1$ for a black body) and σ Stefan-Boltzmann Constant = 5.67051 x 10⁻⁸ W/m²K⁴.

APPENDIX II: Is Heat a property?

To answer this question, consider a bike pump.



Suppose initially, the air inside the pump is at atmospheric conditions, call these p_1 and T_1 . Push the piston forward, what happens?

- Pressure and temperature go up to p_2 , T_2 .
- Work is done **on** the system.

Now, suppose instead, a burner is placed under it, what happens?



- Pressure and temperature goes up
- Heat has been transferred **to** the system.

The experiment can be designed so that, in both cases, the final temperatures and pressures are the same.

- In the first case, the heat input Q = 0 kJ;
- In the second case, the heat input $Q \neq 0 kJ$.

But, we have the same initial and final states but different heat transfers In summary:

- Q (or q) is **not** a property;
- We denote an infinitesimal quantity of heat as δQ (or δq). We do this to draw attention to the fact that Q (or q) is not a property. We reserve the symbol 'd' for **changes in properties**

$$\int_{1}^{2} \delta Q = Q_{1-2}, \quad \int_{1}^{2} \delta q = q_{1-2}$$

• Compare this notation with that used for the change of a property like specific volume

$$\int_{1}^{2} dv = v_2 - v_1$$

Tutorial Questions

- 1. A block with a mass of 1kg is raised a height of 1m; what is the work done? [9.81J]
- 2. A block with a mass of 1kg is pushed along a surface for a distance of 1m. If the coefficient of friction between the block and the surface is 0.2, what is the work done? [1.96J]
- 3. A cylinder contains a gas at an initial pressure and volume of 10bar and 1m³ respectively. The gas is expanded to 2m³ according to the following laws:

i.
$$p = Const.$$
 [1MJ]
ii. $pV = Const.$ [693.1kJ]
iii. $pV^{1.4} = Const.$ [605.5kJ]

Calculate the work done in each case. Which is the largest, and why?

- 4. A spherical balloon has a diameter of 0.3m and contains air at a pressure of 1.5 bar. The diameter of the balloon increases to 0.33m and during this process the pressure is *inversely* proportional to the diameter. Calculate the work done by the air during the process. [0.668kJ]
- 5. A gas is compressed according to the law pV = Const. The initial pressure and volume are 5 bar and $1m^3$ and the work done *on* the air is 170 kJ. Determine the final pressure [7.03 bar]

CHAPTER 3

THE FIRST LAW AND ENERGY TRANSFER

THE CHAPTER COVERS:

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SPECIFIC ENTHALPY $h = u + pv$ AND ENTHALPY $H = U + pV$	Page 3.11
TUTORIAL QUESTIONS	Page 3.13

Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 2 "Energy, Energy Transfer and General Energy Analysis" pages 70-77 and Chapter 4 "Energy Analysis of Closed Systems" pages 169-187.

Introduction

As mentioned in previous notes the first law of thermodynamics gives rise to intrinsic internal energy U. However, it gives no indication to what U actually is other than it being a property of a system. In this respect it is rather similar to the zeroth law which establishes temperature yet gives little insight to what temperature actually is. Further insight about temperature, work heat and energy can be gleaned on consideration of the molecular world. Ouantum mechanics reveals that energy is not continuous but is From this point of view temperature is the parameter that determines the most probable discrete. distribution of populations of molecules over the available energy states of a system at equilibrium. Work on the other hand is a form of energy transfer that makes use of the uniform motion of atoms in the surroundings (movement of piston, lifting of a weight, etc.). Similarly heat is the form of energy transfer that makes use of the random motion of atoms in the surroundings. Thus work is organised energy transfer and heat is random and this distinction is worth bearing in mind. Energy associated with molecules can be viewed in purely mechanical terms (neglecting nuclear and chemical) and U is no more than a measure of the potential and kinetic energy of molecules although classical thermodynamics makes no reference to this fact. It is established in this section that U is a property of the system, i.e. it does not depend on path. Thus whilst energy can be transferred to a system by means of work and heat, once the energy is inside a system then the system has no "knowledge" of how the energy was transferred. The system has no "knowledge" of the past (is not history (path) dependent) which is of course what defines a property. Distinguishing between heat and work is done in the surroundings, i.e. raising or lowering temperature or lifting or lowering a weight.

The First Law of Thermodynamics

The equivalence between work and heat (from the point of view of its effect on a system) was established by Joule between 1840 and 1848. Joule was led to postulate the **First Law of Thermodynamics**.

When a system executes a cyclic process, the algebraic sum of the work transfers is proportional to the algebraic sum of the heat transfers.

This can be written mathematically as:

referred to as the *mechanical equivalent of heat* and C represented a closed contour or a cycle. \tilde{J} is a conversion factor to allow for the different units which may be used for heat and work transfer. In Imperial units $\tilde{J}=778$ ftlb./Btu whilst in SI units $\tilde{J}=1$ since both work and heat are measured in Joules (the SI system is *rational*).



The First Law of Thermodynamics applicable to a cycle is: f(z)

 $\int_{C} \delta Q \propto \int_{C} \delta W$ or $\tilde{J} \int_{C} \Box = \Box \int_{C} \delta W$, where \tilde{J} is a constant

$$\int_{C} \left(\tilde{J} \, \delta Q - \mathcal{F} W \right) = 0$$

Often however, in engineering applications, the system may not undergo a cycle. An example of this might be an air bag in a car.

Clearly, in this case, the airbag does not undergo a cyclic process. For this problem, *how do we perform a thermodynamic analysis on the system*? The answer lies in the fact that, although the relationship $\int_{C} (\tilde{J}\delta Q - SW) = 0$

applies only to cyclic processes, the equation *implies* the existence of a thermodynamic property to be found in the system. That property is called **energy**.

Cyclic Process

Whenever a system undergoes a process, and the state of the system returns to its original values, then the process is called a **cyclic process**. The diagram below illustrates stirring process which raises the temperature of a liquid which is then placed in a bath to return it to its original value. The process $1 \sim 2 \sim 1$ is a cyclic process.



- Raised the temperature the water by work transfer, i.e. by \dot{W}_s
- **Cooled** the water by heat transfer
- As far as the system is concerned, the heat and work transfers are **equivalent** i.e. either process (or a mixture of both) can be made to produce the same changes of state in the working fluid.

Intrinsic Energy U

Consider two cyclic processes 1-A-2-B-1 and 1-A-2-C-1, for a closed system, where X and Y are two independent properties.

t

From the First Law, for the cycle 1-A-2-B-1

$$\int_{1-A-2} (\delta Q - \delta W) + \int_{2-B-1} (\delta Q - \delta W) = 0$$

Similarly for the cycle 1-A-2-C-1
$$\int_{1-A-2} (\delta Q - \delta W) + \int_{2-C-1} (\delta Q - \delta W) = 0$$

Equating these gives
$$\int_{1-A-2} (\delta Q - \delta W) + \int_{2-B-1} (\delta Q - \delta W) + \int_{2-C-1} (\delta Q - \delta W)$$

or
$$\int_{2-B-1} (\delta Q - \delta W) = \int_{2-C-1} (\delta Q - \delta W) = \int_{2-C-1} (\delta Q - \delta W)$$

In view of the fact that neither δQ nor δW is a property, i.e. in general in mathematically terms

$$\int_{2-B-1} \delta Q, \neq \int_{2-C-1} \delta Q, \qquad \int_{2-B-1} \delta W \neq \int_{2-C-1} \delta W$$

It can be immediately inferred that the value of the **combination** of terms $\delta Q - \delta W$ between points 1 and 2 is numerically the same regardless of whether path '*B*' or path '*C*' is traversed. Recalling that a quantity which is independent of the path followed and depends only on the end points is called a property. As a property depends only on the initial and final states it follows that

$$\int_{2-B-1} \left(\delta Q - \delta W \right) = \int_{2-C-1} \left(\delta Q - \delta W \right) = \int_{1}^{2} \left(\delta Q - \delta W \right) = U_{2} - U_{1}$$

where the 1 and 2 refer to the initial and final states, respectively and $U_2 - U_1$ is the change of a thermodynamic property called the **intrinsic internal energy.** This relationship can also be written in incremental form, i.e. $\delta Q - \delta W = dU$.

From the first law of thermodynamics, a number of useful consequences can be derived. These consequences are called *corollaries*.

Corollary 1

There exists a property of a closed system such that *a change in its value* is equal to the net heat and work transfers occurring during any change of state. This property is called **the internal energy** and is denoted by U.

$$Q_{1-2} - W_{1-2} = \int_{1}^{2} \delta Q - \int_{1}^{2} \delta W = U_{2} - U_{1}$$

Corollary 2

The internal energy of a closed system remains unchanged if the system is isolated from its surroundings.

Proof: Isolation, by definition implies work and heat transfers to the system or from the system are zero. Hence $U_2 - U_1 = 0 \implies U = \text{const.}$

Corollary 3

A Perpetual Motion Machine of the first kind (a PMM 1) is impossible.

Proof: We define a *perpetual motion machine of the first kind* as a device that continually produces a net work output without absorbing energy from its surroundings. Schematically, this is depicted as:



From the sketch: $Q_{1-2} = 0$, $W \ge 0$, i.e. work is produced. It follows therefore that

$$-W_{1-2} = U_2 - U_1$$

i.e. to produce work, the internal energy of the system must reduce. To produce work continuously forever (without energy transfer to the system), the internal energy of the system would have to be initially infinite!

The general form of the First Law

A somewhat more general form of the energy equation is

$$Q_{1-2} - W_{1-2} = \int_{1}^{2} (\delta Q - \delta W) = E_2 - E_1 = \Delta E = \Delta (E_p + E_k + U) = \Delta E_p + \Delta E_k + \Delta U$$

where kinetic energy $E_k = \frac{1}{2}mv^2$ & $\Delta E_k = \frac{1}{2}m(v_2^2 - v_1^2)$, potential energy $E_p = mgz$ & $\Delta E_p = mg(z_2 - z_1)$, intrinsic internal energy U = mu & $\Delta U = m(u_2 - u_1)$, which on substitution gives

$$Q_{1-2} - W_{1-2} = m \left\{ g z_2 + \frac{v_2^2}{2} + u_2 \right\} - m \left\{ g z_1 + \frac{v_1^2}{2} + u_1 \right\} = m \left(e_2 - e_1 \right).$$

This is the most general form of the First Law on the 1st year course and on dividing through by m gives

$$q_{1-2} - w_{1-2} = e_2 - e_1$$

where q_{1-2} and w_{1-2} are the *specific* heat and work transfers (i.e. the amount of heat and work transferred per unit mass in the system).

Example Question: Confirm the consistency of the units on the right hand side of the First Law of thermodynamics: $q_{1-2} - w_{1-2} = e_2 - e_1$, where $e = gz + \frac{1}{2}v^2 + u$.

Solution: Recall that, if dealing with specific quantities

Quantity	Units
Intrinsic internal energy (u)	J/kg
Kinetic energy $(\frac{1}{2}v^2)$	m^2/s^2
Potential energy (gz)	$\frac{m}{s^2} \times m$

It is clear that kinetic and potential energies have the same units, i.e. m^2/s^2 . For the internal energy

$$\begin{bmatrix} J \\ kg \end{bmatrix} = \begin{bmatrix} Nm \\ kg \end{bmatrix} = \begin{bmatrix} kgm \\ s^2 \times \frac{m}{kg} \end{bmatrix} = \frac{m^2}{s^2}$$

and hence the units used in the first law are consistent (as expected).

Important points:

- 1. All of the terms have *consistent* units;
- 2. Do not mix units (i.e. specific/absolute etc.);
- 3. Watch for consistency (i.e. do not mix kJ/kg for u with m/s for v).

The differential form of the first law

Up until now, the first law has been written in either of the integral forms

$$Q_{1-2} - W_{1-2} = \int_{1}^{2} (\delta Q - \delta W) = E_2 - E$$
$$q_{1-2} - W_{1-2} = \int_{1}^{2} (\delta q - \delta W) = e_2 - e_1$$

An alternative, equivalent formulation can be written as (in terms of specific quantities)

$$\delta q - \delta w = de = gdz + d\left(\frac{1}{2}v^2\right) + du$$

which is the *differential* form of the first law. The advantage of this latter form is that it is often possible to write δq and δw in terms of state variables and thereby obtain analytic relationships between the heat and work transfers, and the internal energy. One obstacle to this approach is that the process must be <u>quasi-static</u> in order to submit to such an analysis. For example, in the absence of kinetic and potential terms the first law gives

$$\delta q - \delta w = du$$
.

In the case of displacement work $\delta w = pdv$ (the system boundary moves) and the first law gives

$$\delta q - p dv = du$$

which can be integrated to relate the heat transfer to the changes in internal energy and specific volume. However, recall that $\delta w = pdv$ only holds for quasi-static processes - ones in which there are no pressure gradients. If the process is not quasi-static, then $\delta w \neq pdv$, and the previous analytic steps would be invalid.

It is important to appreciate however that the first law is not limited to quasi-static analysis since $Q_{1-2} - W_{1-2} = E_2 - E_1$ is *always* true (it is the conservation of energy).

Rate forms of the First Law

Rate forms of the first law are not directly applicable to quasi-static processes since rates are invariably zero and time is not an explicit feature. Nevertheless change involves the passage of time and a slowly varying process can provide a good approximation of a quasi-static process with finite rates. As mentioned in previous notes (on neglect of kinetic and gravitational potential energy) the differential form of the energy equation for a closed system is $dU = \delta Q - \delta W$. The notation used here (i.e. d and δ) refers to incremental change and change advances with time, hence $dU = \dot{U}dt$, $\delta Q = \dot{Q}dt$ and $\delta W = \dot{W}dt$ with dt an increment of time. Substitution of these expressions into the energy equation reveals the rate form

$$\dot{U} = \frac{dU}{dt} = \dot{Q} - \dot{W}$$

where it is recognised that the time derivative of U is appropriate arising because U is a property, i.e. U is a well defined function. It is generally **incorrect** to replace the heat and work rates \dot{Q} and \dot{W} with

derivatives $\frac{dQ}{dt}$ and $\frac{dW}{dt}$, i.e. $\dot{Q} \neq \frac{dQ}{dt}$ and $\dot{W} \neq \frac{dW}{dt}$, since Q and W are meaningless in general (heat and work are not properties of a system).

Control volume analysis (this is rather tricky)

Consider a control volume identified by all the points in a continuous set Ω and total volume given by the integral $\int_{\Omega} dV$ and surrounded by a boundary Γ whose surface area is the integral $\int_{\Gamma} dA$.



The expectation here is that U can be expressed using a volume integral whilst \dot{Q} and \dot{W} involve surface integrals since we have discovered that heat and work are forms of energy transfer between a system and the surroundings. The expressions are:

$$U = \int_{\Omega} u dm, \ \dot{Q} = \int_{\Gamma} \dot{q} dA \ \text{and} \ \dot{W} = \oint_{\Gamma} \tau \cdot \mathbf{v} dA \ \text{(work rate (power) considered here)}$$

where $dm = \rho dV = \nu^{-1} dV$, ρ is density, \dot{q} is heat flux (rate per unit area-see previous notes) whilst τ is a surface stress (i.e. force per unit area and $d\mathbf{F} = \tau d\mathbf{A}$ - see previous notes). Note that a displacement power flux is of the form stress times velocity.

The rate form of the energy equation is a rather tricky looking equation of the form

$$\frac{d}{dt} \int_{\Omega} u dm = \int_{\Gamma} \frac{\dot{q} dA}{\Gamma} \int_{\Gamma} \tau \cdot v dA \quad (although complicated looking this is simply \dot{U} = \dot{Q} - \dot{W})$$

where $\tau = p\mathbf{n}$ for pressure displacement work.

The energy equation in this form is not examined this year but is presented here to emphasise the distinction between d and δ or equivalently the time derivative and rate, which is readily apparent on contrasting the left and right hand sides of this equation.

Kinetic and potential energy can be readily incorporated to give an even more complex-looking equation, i.e.

$$\frac{\mathrm{d}}{\mathrm{dt}} \int_{\Omega} \left(u + \frac{1}{2} v^2 + gz \right) \mathrm{dm} = \int_{\Gamma} \frac{\mathrm{d}}{\Gamma} \int_{\Gamma} \tau \cdot v \mathrm{dA} \quad (\mathrm{i.e.} \ \dot{\mathrm{E}} = \dot{\mathrm{Q}} - \dot{\mathrm{W}})$$

Applications of the First law to closed systems

Constant volume processes and c_v

Consider a rigid vessel whose volume is effectively invariant.



The vessel is a closed system and is therefore amenable to the first law equations discussed above.

Heating processes in rigid vessels

Suppose heat is transferred to the vessel, so $\delta q > 0$ and evidently no work is done by the system. The energy equation reduces to $\delta q = de$ but the vessel is not moving and suffers no change in elevation so $\delta q = du$ applies. In this instance the change in internal energy of the working fluid is equal to the quantity of heat transferred.

Is there any way we can relate heat transfer to temperature change?

• The temperature change of the working fluid is related to the heat transfer via *the specific heat* capacity at constant volume, c_v

Definition

The specific heat capacity c is defined mathematically as

$$c = \frac{\partial q}{\partial T} \left[\frac{\mathbf{J}}{\mathbf{kgK}} \right]$$

where T is the absolute temperature and $\frac{\partial}{\partial T}$ represents a partial derivative with respect to temperature.

In words, the specific heat capacity is a measure of the amount of heat you have to transfer δq (in order to bring about a temperature change dT).

It is worth pausing for a moment to reflect on the derivative $\frac{\partial q}{\partial T}$ as this appears to suggest that q is

defined, which appears contrary to previous discussions and the use of the symbol δ . Although true in general it transpires q can be defined provided a path is specified (i.e. constant temperature, constant pressure, etc) and the process of change is infinitely slow (i.e. quasi-static). Thus it is *not* enough to define c in isolation since processes can take place at **constant volume** or **constant pressure**, and the process effects the value of the specific heat capacity (since q is path dependent). It is useful to define *two* specific heat capacities;

$$c_{v} = \left(\frac{\partial q}{\partial T}\right)_{v} = \text{specific heat at constant volume}$$
$$c_{p} = \left(\frac{\partial q}{\partial T}\right)_{p} = \text{specific heat at constant pressure}$$

In the vessel above, the volume is constant (v=constant), and the first law provided $\delta q = du$ and hence it follows that on dividing both sides by the incremental temperature dT:

$$c_{v} = \left(\frac{\partial q}{\partial T}\right)_{v} = \left(\frac{\partial u}{\partial T}\right)_{v}.$$

where c_v then is the rate of change of internal energy with temperature, *providing the fluid volume is maintained constant during the process*.

Example Question: A rigid vessel contains a mass of 10kg of a particular fluid. The fluid has a constant specific heat capacity of $c_v = 0.718$ kJ/kgK. If 1 MJ of heat is transferred out of the vessel, calculate the change in temperature of the fluid

Solution: A *rigid* vessel implies dv = 0, therefore, displacement work is zero, and there are no shafts etc. sticking out of the system. It follows that $\delta q = du$. Since $c_v = \left(\frac{\partial u}{\partial T}\right)_v$ the energy equation

 $\delta q = du = c_v dT$ can be integrated to give

$$\int_{1}^{2} \delta Q = Q_{1-2} = m \int_{1}^{2} c_{v} dT = m c_{v} (T_{2} - T_{1}) = m c_{v} \Delta T.$$

since specific heat is a constant in this case. It follows that

$$\Delta T = \frac{Q_{1-2}}{mc_v} = \frac{-1 \times 10^6}{10 \times 718} = -139 K$$

Observe that $\Delta T < 0$, i.e. $T_2 < T_1$, which is expected since the vessel is cooled by the heat transfer.

Pitfalls of the specific heat capacity



This sketch demonstrates pictorially how the specific heat capacity c_v is the gradient of the u-curve on the internal energy-temperature graph.

However, care must be taken since c_v is not always well defined. If for example one considers the boiling of water. What happens when water boils?

- Heat is added.
- There is a *phase change*.
- The temperature stays constant until all of the water has boiled.

This means that during the evaporation process, $\delta q \neq 0$ and

dT = 0 which in turn implies that
$$c_v = \left(\frac{\partial q}{\partial T}\right)_v \rightarrow \infty$$
 for

evaporation. Thus specific heat capacity is not an appropriate concept when dealing with phase changes (more on this later).

Work processes in rigid vessels

Consider again our rigid vessel but in this case shaft work is performed.



The first law applied to this system becomes $\delta q - \delta w_s = du$. Assume further that the vessel has no heat transferred to or from it, i.e. $\delta q = 0$. When a process involves no heat transfer, it is said to be *adiabatic*. For this system, the first law becomes

$$-\delta w_s = \mathrm{d} u$$
.

Notice the negative sign appearing before δw_s .

If work is done **on** the system,

If work is done by the system

$$\delta w_s < 0, \quad \therefore \\ (-\delta w_s) = du > 0$$

$$(-\delta w_s) = du < 0$$

An adiabatic system must draw upon its internal energy to do work, and it can top up its internal energy if work is done on it.

Example Question: A thermally insulated rigid vessel contains a mass of 10kg of a particular fluid. The fluid has a constant specific heat capacity of $c_v = 0.718$ kJ/kgK. It is estimated that 1 MJ of work is transferred to the fluid by means of an impellor. Determine the increase in internal energy and temperature (assumed to be uniform) of the fluid. Heat loss to the surroundings can be ignored.

Solution: The energy equation in this case reduces to $-\delta W_s = dU = mc_v dT$, which can be integrated to give

$$-\int \delta W_{s} = -W_{1-2} = \int_{1}^{2} dU = \Delta U = m \int_{1}^{2} c_{v} dT = m c_{v} (T_{2} - T_{1}) = m c_{v} \Delta T .$$

since specific heat is a constant in the this case. It follows that

$$\Delta T = \frac{-W_{1-2}}{mc_v} = \frac{1 \times 10^6}{10 \times 718} = 139 \text{ K}.$$

and
$$\Delta U = -W_{_{1-2}} = - \left(-1 \!\times\! 10^6 \right) \!=\! 1 MJ$$

Constant pressure processes and c_p

Heating processes in a constant pressure system

Consider having a freely moving piston constrained by a weight, located in a cylinder and enclosing a thermodynamic system.



As the system expands and contracts, the piston will move up and down, thereby maintaining constant pressure in the system. The energy equation for this case is $\delta q - \delta w_D = du$ where in this case there exists a non-zero displacement work term $\delta w_D = pdv$. The energy equation reduces to $\delta q = du + pdv$. But since p is constant $\delta q = du + pdv = d(u + pv) = dh$, where h = u + pv. The quantity h = u + pv is called the specific **enthalpy** of the system. The

The quantity h = u + pv is called the specific **enthalpy** of the system. The actual enthalpy for the system is

$$H = mh = m(u + pv) = U + pV$$

The enthalpy is a very important quantity in thermodynamics, especially in open systems. It is a quantity that automatically captures the displacement work performed in pushing back the surroundings. It is similar to internal energy in that it is a property (being a combination of properties U, p and V) and has the units of energy. Its ability to automatically capture the displacement work done in pushing back the surroundings is particularly convenient and thus has been tabulated for many materials (see steam tables for example).

Similar to the case for constant volume processes, the amount of heat transferred to our constant pressure system can be associated to temperature rise via a specific heat capacitance, i.e. $\delta q = dh = c_p dT$, where

$$c_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p$$
. Integrating the energy equation gives

$$q_{1-2} = h_2 - h_1 = \int_1 c_p dT = c_p (T_2 - T_1)$$

where the last term is obtained with the assumption that c_p is constant (generally it is a function of T).

Work processes in a constant pressure system



In this case, we have both a shaft work *and* a displacement work term appearing in the first law equation. The system is adiabatic, so

$$-(\delta w_{d} + \delta w_{s}) = du$$
$$-\delta w_{s} = d(u + pv) = dh$$
If shaft work is done **on** the system,
$$\delta w_{s} < 0$$
$$(-\delta w_{s}) = dh > 0$$

• If shaft work is done **by** the system $\delta w_s > 0$

$$(-\delta w_s) = dh < 0$$

Example Question: A flexible walled vessel contains a mass of 10kg of a particular fluid is heated at constant pressure. The fluid has a constant specific heat capacity of $c_p = 0.8$ kJ/kgK. If 1 MJ of heat is transferred to of the fluid, calculate the change in temperature of the fluid

Solution: In this case $\delta q = dh$. Since $c_p = \left(\frac{\partial h}{\partial T}\right)_p$ the energy equation $\delta q = dh = c_p dT$ can be

integrated to give

$$\int_{1}^{2} \delta Q = Q_{1-2} = m \int_{1}^{2} c_{p} dT = m c_{p} (T_{2} - T_{1}) = m c_{p} \Delta T.$$

since specific heat is a constant in the this case. It follows that

$$\Delta T = \frac{Q_{1-2}}{mc_p} = \frac{1 \times 10^6}{10 \times 800} = 125 \text{K} \,.$$

Observe that $\Delta T > 0$, i.e. $T_2 > T_1$, which is expected since the vessel is heated by the heat transfer.

Tutorial Questions

<u>General</u>

- 1. A rigid tank contains a hot fluid that is cooled while being stirred by a paddle wheel. Initially, the internal energy of the fluid is 800kJ. During the cooling process, the fluid loses 500kJ of heat, and the paddle wheel does 100kJ of work on the fluid. Determine the final internal energy of the fluid. Neglect the energy stored in the paddle wheel. $[U_2=400kJ]$
- 2. A 50kg iron block at 80°C is dropped into an insulated tank that contains 0.5m^3 of liquid water at 25°C. Determine the temperature of the system when thermal equilibrium is reached. Take the specific heat of iron to be $C_{iron} = 0.45kJ/kgK$ and for water 4.18kJ/kgK. Assume that water has a density of $1000kg/m^3$. [$T_2 = 25.6^\circ C$]
- 3. We all remember being slapped when younger (or perhaps more recently, while entertaining a few close friends). The area being slapped always feels warmer after the blow has been struck. Imagine an angry person slaps you in the face. The slapping causes the temperature of the affected area of your face to increase by 1.8° C. Assume that the mass of the slapping hand is 1.2kg, and that about 0.15kg of the tissue on your face and the hand is affected by the incident. Further assume that the temperature of the slapping hand is unchanged during the process. Estimate the velocity of the hand just before impact. Take the specific heat of the tissue to be 3.8kJ/kgK. [41.4m/s]

Using Pure Substances (covered in Chapter 4)

- 4. A closed tank contains 0.287kg of water and 0.713kg of steam at 7 bar. The tank is heated until is contains only saturated steam. Determine the final pressure and the heat supplied. [10bar, 550kJ]
- 5. A cylinder contains 1kg of water at $5^{\circ}C$ and 6 bar. It is heated at constant pressure until the volume becomes $0.514m^3$. Determine the final conditions and the heat supply. [superheated, 400°C, 3249kJ]
- 6. A tank of volume $0.285m^3$ contains saturated ammonia vapour at $48^{\circ}C$. Calculate the heat transfer when the temperature is decreased to $4^{\circ}C$. [-3623kJ]
- 7. A rigid tank is divided into two equal parts by a partition. Initially, one side of the tank contains 5kg of water at 200kPa and 25° C, and the other side is evacuated. The partition is then removed, and the water expands into the entire tank. The water is allowed to exchange heat with its surroundings until the temperature in the tank returns to the initial value of 25° C. Determine (a) the volume of the tank, (b) the final pressure and (c) the heat transfer for the process. [0.01m³, 3.16kPa, 0.265kJ]
- 8. The expansion of steam in a cylinder follow the law $pV^{1.1} = const$. At the start of the process, the pressure is 2.5 bar and the dryness is 0.9. The expansion ends when the volume is four times the initial volume. Calculate the heat transfer per kg during the process. [52.3kJ/kg]
- 9. Steam expands in a cylinder following the law $pV^n = const$. At the start of the process, the pressure is 6 bar and the temperature is $200^{\circ}C$ and at the end, the pressure is 0.7 bar and the quality is 1.0. Determine the heat transfer per kg. [n = 1.13, q = 206.6kJ/kg]

CHAPTER 4

WORKING FLUIDS: PURE SUBSTANCES (VAPOURS)

THE CHAPTER COVERS:

PURE SUBSTANCES	Page 4.2
PHASE CHANGE	Page 4.2
EQUILIBRIUM SURFACE	Page 4.2
READING STEAM TABLES	Page 4.3
DRYNESS FRACTION (QUALITY)	Page 4.6
THERMODYNAMIC PROPERTIES FOR A WET VAPOUR	Page 4.9
READING EXERCISE: UNDERSTANDING PHASE CHANGE	Page 4.11
TUTORIAL QUESTIONS	Page 4.19

Part of these Notes form a compulsory reading Exercise:

Read: Notes Chapter 4 "Working Fluids: Pure Substances (Vapours)" last nine pages.

Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 2 "Properties of Pure Substances" pages 111-141.

Introduction

Up to this point in the course attention has been directed towards general principles, i.e. Work, Heat and the First Law. However, in order to take on practical problems (analyse heat exchangers, boilers, engines etc.) and perform calculations some understanding of the behaviour and properties of fluids as temperature and pressure varies is required. This section focuses on a particular type of working fluid referred to as a **vapour**. A vapour is an example of a *pure substance*, and includes fluids such as steam, ammonia and refrigerant-12 (R-12).

The three phases of H₂O, which are familiar to us all, are: solid (ice), liquid (water) and vapour (steam). Combinations of these phases can coexist at particular temperatures and pressures and bearing in mind the two-property rule this behaviour can be represented pictorially as an *equilibrium surface* on a $p-\nu-T$ state diagram. Note that an equilibrium surface represents the behaviour of a pure substance at equilibrium which practically means changes that are performed relatively slowly.

The p – v – T Surface



To gain a better understanding of the subject and to gain familiarity with the terminology used the student is directed to the self-learning section on page 11 of these notes. This is a compulsory reading exercise; the material is examinable.

The focus of the remaining notes is on the practicalities of reading steam tables, which require students to have access to:

Thermodynamic and transport properties of fluids (SI units 5th edition) By G.F.C. Rogers and Y. R. Mayhew (Blackwell publishers)

- These are the preferred steam tables for this course.
- Over the next few pages, we will discuss how to read them

Reading Steam Tables

One of the difficulties with dealing with vapours is that their states are **not** usually amenable to simple analytic expression (such as the gas laws). Therefore dealing with vapours for engineering calculations, **requires the use of steam tables**.

Steam tables are a calculation tool. In the case of steam tables, the $p-\nu-T$ surface of a pure substance such as water, ammonia (NH₃) or dichlorodifluromethane (R-12) is tabulated in terms of temperature and pressure.

Recall that in the introductory lectures, the *two property* rule was mentioned. *For any homogeneous thermodynamic system, two properties are sufficient to define entirely the thermodynamic state of that system*. In steam tables, temperature and pressure are used as the reference properties because these are the easiest to use experimentally and practically.



Where to find what for various pure substances in the steam tables (left sketch H_2O , right sketch for other pure substances)

Reading properties for saturated water and steam (pages 2-5)

Along the top of page 2 you will see

$$\begin{bmatrix} T & P_s & v_g & h_f & h_{fg} & h_g & s_f & s_{fg} & s_g \\ \begin{bmatrix} {}^{\mathrm{o}}\mathrm{C} \end{bmatrix} & \begin{bmatrix} \mathrm{bar} \end{bmatrix} & \begin{bmatrix} \mathrm{m}^3/\mathrm{kg} \end{bmatrix} & \begin{bmatrix} \mathrm{kJ}/\mathrm{kg} \end{bmatrix} & \mathrm{kJ}/\mathrm{kgK} \end{bmatrix}$$

Along the top of pages 3-5, you will see

Focusing on the liquid, wet vapour and vapour regions and superimposing isobars on the t - v diagram and isotherms on the p - v gives the following plots.



The dotted line to the left of the critical point is the **saturated fluid line** – any point on this line has the suffix f. The dotted line to the right of the critical point is the **saturated vapour line** – any point on this line has the suffix g. Comparing the entries on pages (3-5) of the steam tables to the t-v sketch gives



Example Questions: (saturation temperature and pressure)

- 1. Find the saturation temperature (boiling temperature) for water at a pressure of 6 bar.
- 2. At what pressure will water at 65°C begin to vaporise?
- 3. What is the saturation temperature of R-12 at 1.004 bar?

Solutions:

- 1. Turn to page 4. Next to the value p = 6 bar is the value $t_s = 158.8^{\circ}$ C. The saturation temperature increases with pressure. Expected because it is more difficult for water molecules to escape the liquid with higher pressures.
- 2. Turn to page 2. Next to the value $t = 65^{\circ}C$ is the value $p_s = 0.2501$ bar. The saturation pressure decreases with decrease in temperature. Expected because at because it is more difficult for water molecules to escape the liquid for lower temperatures (less energy to do so).
- 3. Turn to page 14. Next to the value $p_s = 1.004$ bar is the value $t = -30^{\circ}C$. A material with a saturation temperature lower than $0^{\circ}C$ at atmospheric pressure is evidently desirable for a refrigerant.

Example Questions: (Specific Volumes)

- 4. Find the specific volume of saturated water (v_f) and saturated steam (v_g) at a pressure of 1.01325 bar.
- 5. Find the specific volumes of ammonia (NH_3) in the saturated liquid and vapour states at $28^{\circ}C$ what is the saturation pressure?

Solutions:

- 4. Turn to page 2. Next to the value $p_s = 1.01325$ bar is the value $v_g = 1.673 \text{ m}^3/\text{kg}$. Next turn to page 10. Next to the value $p_s = 1.01325$ bar is the value $v_f = 0.001044 \text{ m}^3/\text{kg}$.
- 5. Turn to page 13. Near to the value $t = 28^{\circ}C$ is the value $v_g = 0.1173 \text{ m}^3/\text{kg}$ along with the saturation pressure $p_s = 10.99 \text{ bar}$. Note that v_f is not given on this page but you are directed to page 23 at the top of the table. At page 23 at 300K is the density $\rho_f = 600 \text{ kg}/\text{m}^3$ and it follows $v_f = \rho_f^{-1} = 600^{-1} \text{ m}^3/\text{kg} = 0.0017 \text{m}^3/\text{kg}$. Note the approximate calculation of v_f here since $t = 28^{\circ}C = 301$ K. Greater accuracy can be achieved with interpolation if necessary.

Interpolation

The steam tables do not contain entries for every possible state point on the p-v-T surface. Therefore, it is often necessary to **interpolate** between values given in the tables. The interpolation is linear as this is accurate enough for engineering calculations.

To recap linear interpolation; suppose we want the value of a function y = f(x) at a given point. All we know are the values of the function at two other adjacent points, between which the desired point lies:



Fitting a straight line between $y_1 = f(x_1)$ and $y_2 = f(x_2)$ gives by means of similar triangles:



$$\frac{y_a - y_1}{x_a - x_1} = \frac{y_2 - y_1}{x_2 - x_1} \text{ or } \frac{y_a - y_1}{y_2 - y_1} = \frac{x_a - x_1}{x_2 - x_1} \text{ or}$$
$$y_a = y_1 + \left(\frac{x_a - x_1}{x_2 - x_1}\right)(y_2 - y_1)$$



Example Question:

Find the saturation temperature of water at a pressure p = 11.5 bar.

Solution:

Turn to page 4. Next to the value p = 11 bar is the value $t_s = 184.1^{\circ}$ C. Moreover, next to the value p = 12 bar is the value $t_s = 188.0^{\circ}$ C. The answer is simply $\frac{184.1+188}{2} = 186.05^{\circ}$ C because $\frac{11+12}{2} = 11.5$ bar but let us use the linear interpolation formula based on similar triangles, i.e. $\frac{t_s - 184.1}{188 - 184.1} = \frac{t_s - 184.1}{3.9} = \frac{11.5 - 11}{12 - 11} = \frac{0.5}{1} \Rightarrow t_s = 184.1 + 3.9 \times 0.5 = 186.05^{\circ}$ C.

Dryness Fraction

Consider a vessel at a given pressure and saturation temperature as depicted in the diagram.



An important question of concern is;

How much of the water has turned to vapour?

or to put it another way;

How <u>dry</u> is the wet vapour?

It is important to appreciate that we are concerned here with a system in equilibrium, i.e. the steam and water have the same temperature and pressure.

This question cannot be answered directly just by reading figures from the steam tables – some additional calculations are required.

Recall that two independent quantities are necessary and sufficient to determine the thermodynamic state of a simple system. However, the complete thermodynamic state of the system includes how much of the water has vaporised. This cannot be determined by knowledge of temperature at pressure alone because during evaporation, **pressure** and **temperature** are NOT independent. Thus, if one is fixed, then so is the other, which is evident on examination of the steam tables and the examples above. To cater for this difficulty a new independent parameter to describe the state of the vaporisation process is introduced, which is denoted the **dryness fraction**.

The **dryness fraction** (or **quality**) is denoted by x and is defined to be:

$$x = \frac{m_g}{m_f + m_g} = \frac{\text{Mass of vapour in the system}}{\text{Total mass in system}}$$

 $x \rightarrow 0 \implies$ fluid is entirely liquid just starting to boil.

 $x \rightarrow l \implies$ fluid is dry saturated vapour just about to enter superheat region.

The dryness fraction is *only* defined in the wet vapour region and by definition $0 \le x \le 1$. It has no meaning to ask for the value of x either in a liquid or a superheated vapour.

Dryness fraction provides the needed measure of how far along the vaporisation process we are in a given problem. From this point on, we use a suffix x to denote quantities at a given/desired dryness fraction x



Consider a closed system of volume V containing H_20 in the form of a wet vapour. The mass of the wet vapour is $m = m_f + m_g$. The volume V, internal energy U, enthalpy H, entropy S can be expressed by the formulae:

$$V = mv_x = m_f v_f + m_g v_g \Longrightarrow v_x = \frac{m_f}{m} v_f + \frac{m_g}{m} v_g = (1 - x) v_f + xv_g = v_f + x (v_g - v_f)$$

$$U = mu_x = m_f u_f + m_g u_g \Longrightarrow u_x = \frac{m_f}{m} u_f + \frac{m_g}{m} u_g = (1 - x) u_f + xu_g = u_f + x (u_g - u_f)$$

$$H = mh_x = m_f h_f + m_g h_g \Longrightarrow h_x = \frac{m_f}{m} h_f + \frac{m_g}{m} h_g = (1 - x) h_f + xh_g = h_f + x (h_g - h_f) = h_f + hv_{fg}$$

$$S = ms_x = m_f s_f + m_g s_g \Longrightarrow s_x = \frac{m_f}{m} s_f + \frac{m_g}{m} s_g = (1 - x) s_f + xs_g = s_f + x (s_g - s_f) = s_f + xs_{fg}$$

Each of these equations offers a formula for determining the dryness fraction x, i.e.

$$x = \frac{v_x - v_f}{v_g - v_f} \quad \text{or} \qquad x = \frac{u_x - u_f}{u_g - u_f} \quad \text{or} \qquad x = \frac{h_x - h_f}{h_{fg}} \quad \text{or} \qquad x = \frac{s_x - s_f}{s_{fg}}$$

Example Question: Find the specific volume of wet steam with a quality of 67% at a pressure of 6 bar.

Solution: From the question x = 0.67. The vapour is evidently wet. Examination of page 4 at reveals at p = 6 bar the value $t_s = 158.8^{\circ}$ C and $v_g = 0.3156 \text{ m}^3/\text{kg}$. The specific volume v_x is provided by the formula $v_x = v_f + x(v_g - v_f)$ but to apply this formula v_f is needed. There are three approaches one can adopt to obtain v_f .

1. Assume
$$v_f = \frac{1}{\rho} = 1000^{-1} \frac{m^3}{kg} = 0.001 \frac{m^3}{kg}$$
 for water.

2. Find v_f from page 10 of steam tables, which $v_f = 0.001102 \frac{\text{m}^3}{\text{kg}}$.

3. Appreciate that $v_f \ll v_g$, so simply ignore it.

Using each of these three methods gives slightly different answers:

1.
$$v_x = 10^{-3} + 0.67(0.3156 - 10^{-3}) = 0.2118 \text{ m}^3/\text{kg}$$

2.
$$v_x = 0.1102 \times 10^{-2} + 0.67 (0.3156 - 0.1102 \times 10^{-2}) = 0.2118 \text{ m}^3/\text{kg}$$

3.
$$v_x = 0.67(0.3156) = 0.2115 \,\mathrm{m^3/kg}.$$

Example Question: Find the state (temperature and dryness fraction) of steam at 12 bar, with a specific volume of $0.1 \text{m}^3/\text{kg}$.

Solution: From tables on p.4, at 12 bar, $v_g = 0.1632 \frac{\text{m}^3}{\text{kg}}$ and $v_f \approx \frac{1}{1000} \frac{\text{m}^3}{\text{kg}}$.

The specific volume given is $v_x = 0.1 \frac{\text{m}^3}{\text{kg}}$ and it is evident that $v_f \le v_x \le v_g \iff 0 \le x \le 1$, which infers that the steam is wet. The saturation temperature $t_s = 188^\circ \text{C}$ and the dryness fraction

$$x = \frac{0.1 - 1/1000}{0.1632 - 1/1000} = 0.61.$$

Finding other thermodynamic properties for a wet vapour

Example Question: Find the internal energy of steam at 40 bar, with a dryness fraction of 0.6.

Solution: Use the formula $u_x = u_f + x(u_g - u_f)$ where the u's are taken from the 40 bar row on page 4. Thus , $u_x = 1082 + 0.6(2602 - 1082) = 1994 \text{kJ/kg}$.

Example Question: Steam is at a pressure 16 bar and has an internal energy of

- (i) 2432 kJ/kg;
- (ii) 2700 kJ/kg.

For both cases, find out if the vapour is wet or superheated and where appropriate, find the dryness fraction.

Solution: On page 4 at p = 16 bar $u_f = 857 \text{ kJ/kg}$ and $u_g = 2596 \text{ kJ/kg}$ hence case (ii) is a superheated vapour. The dryness fraction in case (i) is simply $x = \frac{u_x - u_f}{u_g - u_f} = \frac{2432 - 857}{2596 - 857} = 0.906$.

Bilinear Interpolation

When dealing with superheated vapours it is observed that the entries in the tables are quite widely spaced. Often it is necessary to use **bilinear** interpolation, i.e. interpolation on two variables (p & t).

Example Question: Find the internal energy of steam at a pressure of 16 bar and a temperature of 380°C The following readings from page 7 are pertinent.

At p = 15bar, $u_{350} = 2868 \text{ kJ/kg}$ and $u_{400} = 2952 \text{ kJ/kg}$. It follows that. $\frac{u_{380} - u_{350}}{u_{400} - u_{350}} = \frac{u_{380} - 2868}{2952 - 2868} = \frac{380 - 350}{400 - 350} = \frac{3}{5} \Longrightarrow u_{380} = 2868 + \frac{3}{5} \times 84 = 2918.4 \text{ kJ/kg}$

At p = 20bar, $u_{350} = 2861 \text{ kJ/kg}$ and $u_{400} = 2946 \text{ kJ/kg}$. Similarly

 $\frac{u_{380} - u_{350}}{u_{400} - u_{350}} = \frac{u_{380} - 2861}{2946 - 2861} = \frac{380 - 350}{400 - 350} = \frac{3}{5} \Longrightarrow u_{380} = 2861 + \frac{3}{5} \times 85 = 2912 \text{kJ/kg}$

It follows therefore at p = 16bar that

 $\frac{u_{380} - 2918.4}{2912 - 2918.4} = \frac{16 - 15}{20 - 15} = \frac{1}{5} \Longrightarrow u_{380} = 2918.4 - \frac{1}{5} \times \frac{32}{5} = 2917.1 \text{kJ/kg}$

Reading Other Properties from the Steam Tables

Example Question: Find the enthalpy and entropy for R-12 at a pressure of 0.2998 bar, and a quality of 60%.

Solution: From page 14: $h_x = h_f + x(h_g - h_f) = -13.14 + 0.6(162.62 - (-13.14)) = 92.32 \text{ kJ/kg}$ and $s_x = s_f + x(s_g - s_f) = -0.0582 + 0.6(0.7475 + 0.0582) = 0.4252 \text{ kJ/kgK}$.

Example Question: Find the enthalpy of steam at a pressure of 8 bar. With an entropy of 6.5 kJ/kgK. Is the steam wet or superheated? Give reasons for your answer.

Solution: Look at steam at 8 bar on p.4, we find

$$s_f = 2.046 \text{ kJ/kgK}$$

 $s_\sigma = 6.663 \text{ kJ/kgK}$

The entropy given in the question is $s_x = 6.5 \text{ kJ/kgK}$ and observe that $s_f \le s_x \le s_g$. Therefore, the steam is wet and $0 \le x \le 1$. It follows that $x = \frac{s_x - s_f}{s_g - s_f} = \frac{s_x - s_f}{s_{fg}} = \frac{6.5 - 2.046}{4.617} = 0.96$.

Moreover, $h_x = h_f + x h_{fg} = 721 + 0.96(2048) = 2687.1 \text{ kJ/kg}$

READING EXERCISE: UNDERSTANDING PHASE CHANGE

Introduction

This section focuses on a particular type of working fluid referred to as a **vapour**. A vapour is an example of a *pure substance*, and includes fluids such as steam and refrigerant-12. Another class of pure substances used in engineering applications (examined later in the course) are **ideal gases**. Ideal gases are treated differently to fluids.



Pure substances

A pure substance is one which is:

a. homogeneous in composition: this means it has the same ratios of atoms throughout the system, i.e. the composition is the same

b. homogeneous in chemical aggregation: this means it has the same atomic structure, which means that the molecules must be built up in the same way

c. invariable in chemical aggregation: this means that no chemical changes take place with time, i.e. the compound is stable.

Example 1: mixture of all phases of H₂O

This is a pure substance because the system contains only water with the molecules bound together in the same way throughout.

Example 2: air

A mixture of liquid and gaseous air is **not** a pure substance because the molecules are not all the same, and also the equilibrium compositions in the liquid and gas phases will differ due to the difference in boiling points of the constituents, i.e. oxygen and nitrogen

Phases of a pure substance

The major phases of pure substances are solid, liquid and vapour. Substances may exist in two or more phases in equilibrium. This course will concentrate mostly on water (H_2O), for which the following phases can co-exist in equilibrium:

- i. ice (solid) + water (liquid)
- ii. ice (solid) + steam (vapour)
- iii. water (liquid) + steam (vapour)
- iv. ice (solid) + water (liquid) + steam (vapour)

The transitions between these phases have the following names:

- i. transition between water and ice fusion
- ii. transition between ice and vapour phase sublimation
- iii transition between water and vapour phase vaporisation

Phases and transformations are discussed later in the course.

Experiment



Take a kettle, and fill it with water from the tap, plug it in. At time = 0, the water temperature = 20° C. We switch the kettle on. What happens?

• Water starts to heat up.

How much will the water 'heat up' (how far will its temperature continue to change)?

• Until it boils.

What happens during boiling?

Some of the water **changes phase** from *liquid* to *vapour*.

Why does the temperature in the kettle remain constant during boiling?

• Because the energy transferred to the kettle goes toward changing the *phase* of the fluid.

- The temperature at which water boils is dependent upon atmospheric pressure. The higher the **pressure**, the higher the temperature at which boiling takes place.
- This is one of the reasons you cannot make a decent cup of tea on the top of Everest (The boiling point of water there is about 70° C).



The temperature and pressure at which water boils are referred to as *saturation temperature* and *saturation pressure*. The 'saturation' refers to the fact that the fluid is saturated with energy – any further transfer of energy brings about a change of phase.

Suppose we perform a new experiment in which we plot temperature t (in ^oC) against specific volume v for a heating process *similar* to that which takes place in a kettle. The difference between this experiment and the one above is that none of the vapour is allowed to escape through a spout. Also, we will allow the volume of our new vessel to change, in order that the pressure within the system be maintained constant.



The water in the system is initially at 20° C, and the specific volume is v_1 , where

$$v_1 = \frac{1}{\rho_1} \approx \left(\frac{1}{1000}\right) \frac{\mathrm{m}^3}{\mathrm{kg}}$$

It is useful to plot the process on a *t*-*v* diagram.



The system initially occupies the state point (v_1, t_1) . Heat is transferred to the system. As the water warms, it expands slightly.

Chose v_2 to be that point **just** where the water is boiling. At this point $t_2 = t_s$ and $v_2 = v_f$.

In words, this means 'the water is at the saturated (boiling) temperature for the given pressure, its specific volume is that of a **saturated fluid** (i.e. a fluid just beginning to vapourise)'.

What happens if we continue to transfer heat to the system?

- Some of the water vapourises, it becomes steam.
 - Steam is **much less** dense than water. To maintain the same pressure the system must expand – the piston moves up.
- The water and the steam co-exist in equilibrium. This means that if the heat supply is cut off and the system is insulated, the proportions of steam and water remain the same.





•

What happens at state point (5)?

At State point (5), all of the water has been turned to vapour. At this point, the vapour is said to be **dry saturated** – it is saturated in as much as all of the energy which could be accommodated by phase change *has* been accommodated by phase change. The specific volume at state point (5) is denoted

$$V_5 \equiv V_s$$

where the 'g' stands for "dry saturated vapour" (!). If heat is further added at state point (5), the vapour becomes superheated, and both the temperature and the specific volume increase. So, when heating water which is initially @ 20°C (say) to a superheated vapour, we recognise a number of important points:



It is important to emphasise that this curve is for *constant pressure* heating. The amount of energy required to go from saturated liquid to saturated vapour is called *latent heat of vapourisation*.

Suppose we construct a family of these curves, each one corresponding to a different ambient pressure. What we would observe is that as the pressure increases, the onset of boiling is delayed, i.e. the saturation temperature increases. The specific volume of the fluid at the point at which boiling begins also increases. We note also that with an increase in pressure, the region in which vaporisation takes place shrinks, i.e. $v_{fe}(=v_e - v_f)$ decreases with increasing pressure;



The dotted line represents the locus of two sets of points, separated by the **critical point**. To the left of the critical point is the *saturated liquid line*. This is the locus of all the different v_f 's which occur at the saturation temperatures for a given set of pressures. To the right of the critical point is the *saturated vapour line*, which represents the set of v_g 's associated with a given set of saturation temperatures and pressures.

At the **critical point**, v_f and v_g are the same, and the distinction between liquid and vapour is lost. Above the critical point on the *t*-v diagrams, the state of the fluid (liquid, wet vapour, superheated vapour etc. cannot be identified.

Suppose now we examine freezing (instead of boiling) on the *t*- ν diagram. We again start with water at 20°C, l bar, but this time allow it to cool:



In the case of water, the temperature and specific volume decrease up until freezing occurs. Upon freezing (actually, below 4°C) water expands– most other liquids contract.



The fact that water expands on freezing is the reason why domestic plumbing suffers from ruptured pipework in winter.

Just as we did for boiling points, we can construct the locus of the set of freezing points for different ambient pressures;

Here we have shown the vaporisation lines (AB) and the freezing lines (CD).



In summary, we can construct the entire T- ν diagram for water, ranging from the frozen state to superheated steam.



On the sketch are all the features we have so far discussed, plus a new one; the triple point. The triple point for a pure substance is that particular temperature and pressure for which the substance can exist simultaneously in 3 states; solid, liquid and gas. For water at the triple point, we would find blocks of ice floating in liquid water and surrounded by vapour.

Finally, we have marked in the previous diagram the phase transformation process that can occur:

- 1. Vaporisation the liquid phase changes to a vapour (boiling).
- 2. Fusion the solid phase changes to liquid (thawing).
- 3. Sublimation the solid phase changes to vapour (weird).
We can see sublimation in action in winter. Snow which has lain on the ground for a long period of time can appear to vanish without thawing and soaking the ground. This is because the snow sublimates due to the small amount of water in the atmosphere. Sublimation occurs in low humidity climates. The opposite phenomenon also occurs in winter and is called a **hoar frost**.

For a substance other than water, the t-v diagram appears



Other Ways of Examining Pure Substances

As well as plotting the behaviour of a fluid as its temperature increases and its pressure remains the same, we can also plot fluid behaviour as pressure changes and temperature remains the same.

We do this by imagining we have a cup filled with water at 90°C, initially at sea level. The cup is well insulated. Next, we start to climb Mount Everest. As we climb the pressure drops, and the specific volume increases:



Now, recall that at the top of Everest, water boils at 70°C because the atmospheric pressure is very low (~0.3 bar). Our cup contains water at 90°C, so somewhere on the ascent of Everest, the pressure drops to the point where the boiling temperature equals that of the cup of water. Even though we have done nothing to add energy to the cup, the water in the cup starts to boil. **It boils at 90°C.**

We stay where we are on the mountain, while the water boils away. Analogous to the saturation temperature t_s which we discussed in conjunction with the *t*-*v* diagram, we denote by p_s the saturation pressure. This is the pressure at which a pure substance of a given temperature will start to boil. We imagine that our cup is sealed (so that no fluid escapes), and that it can change volume freely so that the pressure inside is the same as the ambient pressure.



Once the cup has boiled dry and contains only vapour (steam), we resume our climb. The pressure drops ever lower and, in effect, our vapour at 90°C becomes more and more superheated for that ambient pressure.

Again, we can construct the locus of points for a given family of temperatures, and we obtain



As in the *t*- ν diagram, we have a critical point, separating the saturated liquid and vapour lines. We can also identify liquid, wet vapour and superheated vapour regions.

Tutorial Questions

- 1. A vessel, volume 10m³, contains 40kg of liquid water and water vapour in equilibrium at 7.0 bar. Calculate
 - a. the dryness fraction, [0.9161]
 - b. volume and mass of vapour, [9.995 m³, 36.6 kg]
 - c. volume and mass of liquid. $[4.6 \times 10^{-3} \text{ m}^3, 3.36 \text{ kg}]$
- 2. A closed vessel contains ammonia vapour, dryness 0.7 at 16°C. The ammonia is heated until it has dryness 0.9. What is the final temperature and pressure? [24°C, 9.7 bar]
- 3. In the following table for steam each column is a separate example. Complete each column omitting any properties which do not apply.

Parameter/Question	1	2	3	4	5	6	7	8
Mass kg	3	4		10				1
Total volume m ³			20	1	220	10	2	
Specific volume					70			
m ³ /kg								
Pressure bar	6.0	7.0	15.0	15.0			8.0	18.0
Temperature °C			350			70		
Degree of superheat		85						
Quality	0.8				1.0	1.0	0.8	.01

4. Determine the quality of the following substances in the given states:

a.	Ammonia	40°C	0.07 m ³ /kg	[x = 0.837]
b.	Freon 12	6.52 bar	0.02 m ³ /kg	[x = 0.736]
c.	Water	40°C	1 m ³ /kg	[x = 0.051]
d.	Water	180 bar	0.007 m ³ /kg	[x = 0.909]

- 5. The radiator of a steam heating system has a volume of 0.2m³ and contains saturated vapour at 1.5 bar. The valves are closed and by cooling the pressure drops to 1.4 bar. Calculate
 - a. the total mass in the radiator, [0.173kg]
 - b. the volume and mass of water in the final state, $[1 \times 10^{-5} \text{ m}^3, 0.01 \text{ kg}]$
 - c. the volume and mass of steam in the final state. [0.19999 m³, 0.1623 kg]
- 6. Steam at the critical state is contained in a rigid vessel. The vessel cools until the pressure is 27.5 bar. Calculate the final quality. [x = 0.0302]
- 7. A rigid vessel contains water and steam at 1.0 bar. Determine the proportion by volume of water and steam necessary to make it pass through the critical state when heated. $[v_g = 2.12 \times 10^{-3} \text{ m}^3/\text{kg}, v_f = 1.04 \times 10^{-3} \text{ m}^3/\text{kg}]$

CHAPTER 5

OPEN SYSTEMS AND ENERGY TRANSFER

THE CHAPTER COVERS:

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TUTORIAL QUESTIONS	Page 5.14

Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 5 "Mass and Energy Analysis" pages 212-242.

Introduction

The thermodynamic analyses undertaken thus far have been based on **closed systems**, i.e. ones in which there is no mass flux across the system boundaries. The following various mathematical forms of the energy equations have been considered:

(i) Integrated form

$$E_{2} - E_{1} = \left\{ U_{2} + mgz_{2} + \frac{1}{2}mv_{2}^{2} \right\} - \left\{ U_{1} + mgz_{1} + \frac{1}{2}mv_{1}^{2} \right\} = Q_{1-2} - W_{1-2}$$

(ii) Differential form

$$dE = d\left(U + mgz + \frac{1}{2}mv^{2}\right) = \delta Q - \delta W$$

(iii) Rate form

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega} \left(u + \frac{1}{2}v^2 + gz \right) \mathrm{d}m = \int_{\Gamma} \frac{\mathrm{d}t}{\Gamma} \tau \cdot v \mathrm{d}A$$

or

$$\frac{dE}{dt} = \frac{d}{dt} \left(U + mgz + \frac{1}{2}mv^2 \right) = \dot{Q} - \dot{W}$$

which all can be divided through by mass m (since m is constant for a closed system) to reveal similar looking equations involving specific quantities.

Transport equations for open systems

The equations above do not account for changes in energy due to mass entering or leaving the control volume Ω through the boundary Γ . However, this is readily accounted by considering an element area dA at control surface Γ . The elemental volume of material exiting at dA is $\mathbf{v} \cdot \mathbf{n} dA dt$ from which it can be deduced that the elemental mass exiting is $\rho \mathbf{v} \cdot \mathbf{n} dA dt$ and it immediately follows that the elemental energy exiting is $\rho \mathbf{v} \cdot \mathbf{n} dA dt$.



The rate form of the energy equation for an open system follows at is

$$\frac{dE_{ev}}{dt} + \int_{\Gamma} ed\dot{m} = \dot{Q} - \dot{W}$$

which is known as the **unsteady flow energy equation** (USFEE), where $e = u + \frac{1}{2}v^2 + gz$ and for the case of a stationary control volume $d\dot{m} = \rho m ndA$.

Many situations arise where energy within the control volume Ω is unchanging, i.e. $\dot{E}_{cv} = 0$ and the resulting equation is

$$\int_{\Gamma} e d\dot{m} = \dot{Q} - \dot{W}$$

which is known as the steady flow energy equation (SFEE).

Many engineering applications **do** have mass flows across their boundaries (i.e. open systems). Examples of this type of system include:

- Boilers
- Aircraft engines
- I.C. engines
- Heat exchangers.

Simplified forms of the flow energy equations

The analysis above revealed that the elemental mass exiting a control volume Ω through the boundary Γ is dmdt = $\rho m ndAdt$, where dm = $\rho m ndA$ and the dot signifies rate. A transport equation for mass is

$$\frac{\mathrm{d}}{\mathrm{dt}}\int_{\Omega} \mathrm{dm} + \int_{\Gamma} \mathrm{d}\dot{m} = 0 \quad \text{or} \quad \dot{m}_{\mathrm{cv}} + \oint \mathrm{d}\dot{m} = 0 \quad \text{or} \quad \dot{m}_{\mathrm{cv}} \pm \dot{m}_{\mathrm{e}} - \dot{m}_{\mathrm{f}} = 0$$

where for the last equation mass is assumed to enter at an inlet and exit at outlet denoted by a suffix 'i' for inlet and 'e' for exit.

The exact same approach applies to the USFEE, i.e. $\dot{E}_{cv} + \oint ed\dot{m} = \dot{Q} - \dot{W}$, which is simplifies to

$$\dot{E}_{ev} + \dot{m}_{ee} - \dot{m}_{e} = \dot{Q} - \dot{W}$$

with exit and inlet identified.

This simplifies even further for the SFEE to $\dot{\mathbf{m}} [\![\mathbf{e}_{e} - \mathbf{e}_{i}]\!] = \dot{\mathbf{Q}} - \dot{\mathbf{W}}$, since for steady flow $\dot{\mathbf{m}} = \dot{\mathbf{m}}_{e} = \dot{\mathbf{m}}_{i}$ (since $\dot{\mathbf{m}}_{ev} = \mathbf{0}$).

Identifying shaft and displacement work rates at Γ gives $\dot{W} = \dot{W}_{s} + \dot{W}_{D} = \dot{W}_{s} + \oint_{\Gamma} pv d\dot{m}$, which on substitution into the USFEE yields

$$\dot{E}_{cv} + \int \dot{W}_{s} \dot{n} = \dot{Q} - \dot{W}_{s}$$

where $e^h = e + pv = u + pv + \frac{1}{2}v^2 + gz = h + \frac{1}{2}v^2 + gz$,

and where h is specific enthalpy. On identifying exits and inlets the USFEE simplifies to

$$\dot{E}_{cv} + \dot{m}_{e}e_{e}^{\dagger} - me_{h}^{\dagger} = \dot{Q} - \dot{W}_{s}$$

Differential forms are obtained on multiplication by dt to give

$$\dot{E}_{cv}dt \pm \int dt dt dt dt = \dot{Q} dt = \dot{W}_{s}dt \Rightarrow dE_{cv} + \int e^{h}d(\delta m) = \delta Q - \delta W_{s}$$

Can you appreciate the reason for the use of the symbol δ in the expression $\delta m = \dot{m}dt$?

Example:

Find the units of the displacement work term.

$$\begin{bmatrix} \dot{m}pv \end{bmatrix} = \begin{bmatrix} kg \\ s \end{bmatrix} \times \begin{bmatrix} N \\ m^2 \end{bmatrix} \times \begin{bmatrix} m^3 \\ kg \end{bmatrix} = \begin{bmatrix} Nm \\ s \end{bmatrix} = \begin{bmatrix} J \\ s \end{bmatrix} = \begin{bmatrix} W \end{bmatrix}$$

The meaning of the displacement work and unsteady terms in the USFEE

In the previous derivation, the displacement work δW_D is taken over to the left hand side of the energy balance. In order to appreciate the reason for this let us examine briefly the meaning of the pv term appearing in the USFEE. The term pv arises from the **displacement work**, but displacement of what?



The displacement refers to the working fluid, which (here) is displaced from outside the device to inside the device. Imagine for a moment that the mass of fluid δm_i is encased in a piston/cylinder arrangement.



In order to get the elemental mass δm_i into the system, the piston must overcome the resisting force produced by the pressure inside the system. Remember, work can only be done against a resisting force and hence (if p = constant)

 $\delta W_{\rm D} = \delta m p_{\rm i} v_{\rm i}$

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Now, in our example the piston is replaced by the upstream flow so δW_D is the work done by the fluid on the system in pushing an elemental mass δm_i of the working fluid across the system boundary.

As mentioned in previous notes enthalpy automatically captures the displacement work performed in pushing back the surroundings.

The term pv is referred to as displacement work, specific flow work or pressure work.

Specific forms of the energy equations

The simplified rate form of the USFEE is

$$\dot{E}_{cv} + \dot{H}_{cv} \left[\begin{array}{c} & \Psi_{s}^{2} \\ 2 & \end{array} \right] \cdot \left[\begin{array}{c} & \Psi_{s}^{2} \\ 2 & \end{array} \right] = \dot{Q} = \dot{W}_{s} \quad [W]$$

which for the steady state case reduces (since $\dot{E}_{cv} = 0$ and $\dot{m}_e = \dot{m}_1 = \dot{m}$) to

$$\dot{m} \left\{ h_{\underline{w}} \underbrace{\underbrace{\mathbf{w}}_{s}^{2}}_{2} \underbrace{\mathbf{w}}_{s} \right\} \xrightarrow{i} \left[\underbrace{\mathbf{w}}_{s}^{2} \underbrace{\mathbf{w}}_{s} \right] = \dot{\mathbf{Q}} = \dot{\mathbf{W}}_{s} \quad \left[\mathbf{W} \right]$$

which reduces further on dividing through by \dot{m} to

$$\left\{h_e + \frac{v_e^2}{2} + gz_e\right\} - \left\{h_i + \frac{v_i^2}{2} + gz_i\right\} = \frac{\dot{Q} + \dot{W}_s}{m - m} = \frac{Q}{m} \cdot \frac{\dot{W}_s}{m} \cdot \frac{1}{m} \cdot \frac$$

where in this equation, q and w_s are taken to mean the heat and shaft work transfers which take place per kg of mass passing through the control volume.

The steady flow energy equation (SFEE) can also be written in a differential form, in much the same way as it was for closed systems, i.e.

$$dh + vdv + gdz = \delta q - \delta W_s$$

Rather interestingly this equation in the absence of shaft work ($\delta w_s = 0$) and assuming adiabatic ($\delta q = 0$) along with isothermal incompressible flow (du = 0, $d\rho = 0$) gives

$$dh + vdv + gdz = d\left(\frac{p}{\rho} + \frac{v^2}{2} + gz\right) = 0 \Longrightarrow \frac{p}{\rho} + \frac{v^2}{2} + gz = const.$$

which is Bernoulli's equation (met in 1st year fluids).

Bernoulli's equation arises here because thermodynamic quantities have essentially being removed leaving only mechanical energy terms which arise in the mechanical-energy form of the momentum equation (not considered further here).

Applying the steady flow energy equation

Adiabatic machines

Recall from earlier lectures that the term 'adiabatic' refers to a process in which there is no heat transfer. Examples of machines that are almost adiabatic (i.e. heat transfer is low relative to flow of energy), and that are common to engineering processes are *compressors* and *turbines*

1) Compressors



Compressors are found in jet engines, air receivers, good quality paint sprayers and fridges, as well as many other applications. As the name implies, a compressor is designed to compress gas i.e. to raise gas pressure. Schematically, a compressor is as shown in the diagram.

Compressors do work on the fluid and hence $\dot{W}_{\rm S} < 0$. Applying the SFEE to the compressor, in terms of specific quantities gives

$$(h_2 - h_1) + \frac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1) = q - w_s$$

Common assumptions for a compressor are: $\frac{1}{2}\Delta v^2 \ll \Delta h$, $g\Delta z \ll \Delta h$ along with adiabatic q = 0 assumption yields a simplified SFEE, i.e.

$$h_1 - h_2 = w_s$$

In a situation where the compressor is compressing an ideal or perfect gas (to be defined later), then the relation $h_1 - h_2 = c_p (T_1 - T_2)$ applies and the following is obtained:

$$\mathbf{w}_{s} = \mathbf{c}_{p} \left(\mathbf{T}_{1} - \mathbf{T}_{2} \right)$$

A compressed gas typically warms up (think of a bicycle pump, or the fuel/air mixture in a diesel engine), which infers that $T_2 > T_1$ and since $c_p > 0$, it follows that

$$w_{s} = c_{p} (T_{1} - T_{2}) < 0$$

which confirms our earlier statement that compressors are power consumers.

Note that the step $h_1 - h_2 = c_p (T_1 - T_2)$ can generally only be made for an ideal or perfect gas. When dealing with a vapour power turbine (i.e. one using steam or similar fluid), one must use steam tables to find the enthalpies at the inlet and exit of the system.

2) Pumps

A similar device to a compressor is a **pump**, which finds applications where liquid is required to be circulated. The pump achieves this by using work to increase the pressure in the liquid. The SFEE for a pump is identical to a compressor but

$$-w_{s} = h_{2} - h_{1} = u_{2} - u_{1} + (p_{2}v_{2} - p_{1}v_{1}) \approx v(p_{2} - p_{1})$$

since $u_2 \approx u_1$ (since little temperature change in liquid) and $v = v_1 \approx v_2$ (liquids are close to incompressible).

Example Question:

A refrigerator compressor is used to compress Freon-12 (R-12) at a mass flow rate of 5 kg/s, with a pressure change from 1.004 bar to 27.89 bar. Calculate the adiabatic power required by the machine. Assume that the condition of the gas is dry saturated at inlet and outlet, and neglect changes in potential and kinetic energy.



Solution: The power requirement is the rate of doing work, i.e. kJ/s, and hence it is \dot{W}_s . Thus the power is

$$-\dot{\mathbf{W}}_{s}=\mathbf{n}_{1}\mathbf{h}_{2}-\mathbf{h}_{1},$$

where h_2 and h_1 can be found from the tables for R-12. This gives

$$-\dot{W}_{s} = i \frac{h_{1}}{h_{2}} = h_{1} = 5 \times (212.8 - 174.2) = 193.0 \text{kW}$$

which means that $\dot{W}_s = -193 kW$.

The significance of the negative sign is that *work is done on the system* in a compressor.

3) Turbines

Turbines are found in jet engines and ground based power producing plant. A turbine is designed to extract energy from the working fluid and convert it to shaft work. Schematically, we represent a turbine as



Note how that a turbine is drawn the opposite way around to a compressor.

Turbines are power producers, i.e. $\dot{W}_s > 0$. Applying the SFEE to a turbine,

$$q - w_s = (h_2 - h_1) + \frac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1)$$

Again assume: $\frac{1}{2}\Delta v^2 \ll \Delta h$, $g\Delta z \ll \Delta h$ along with adiabatic q = 0 assumption yields a simplified SFEE, i.e.

$$w_s = h_1 - h_2$$

Is the adiabatic assumption accurate?

The turbine itself is very hot (it would burn you if you tried to touch the casing). However, the heat transfer 'leakage' through the casing is very small compared to the energy flux through the turbine. Hence q = 0 is a good approximation to the real device.

For the case of a gas turbine $w_s = c_p (T_1 - T_2)$. Now, an expanding gas cools as it flows across the turbine and hence $w_s = c_p (T_1 - T_2) > 0$, confirming the turbine as a power producer. As with compressors, if you are dealing with a vapour power turbine, steam tables must be used to find h_1 and h_2

Example Question:

A steam turbine is supplied with superheated steam at 100 bar, 600°C. The exhaust pressure from the turbine is 6 bar and the temperature is 200°C. Calculate the power output of the turbine if the mass flow rate is 100 kg/s, and the inlet and outlet velocities are equal.

Solution: The enthalpy at states 1 and 2 can be evaluated from the superheat tables. Turn to page 8 at $(p_1, T_1)=(100\text{ bar}, 600^\circ\text{C})$ $h_1 = 3624\text{ kJ/kg}$ and on page 7 at $(p_2, T_2)=(6\text{ bar}, 200^\circ\text{C})$ $h_2 = 2851\text{ kJ/kg}$.



4) Throttling process

Throttling processes occur commonly in engineering, when a fluid is passed from a high pressure to a lower one. An example of a throttling process is the induction system of a petrol engine, when the power output (or speed) of the engine is reduced by fitting a valve in the inlet manifold. Other examples are valves fitted in pipes to control the flow of fluid along the pipe; a stop-cock in a water main might act as a throttle when it is not fully open. Another common example is an *orifice plate* which, as the name suggests, is simply a plate with a carefully sized hole in it designed to regulate the flow rate to a pre-set amount. When the working fluid is a pure substance, the sharp pressure drop produced across a throttle can result in a sharp temperature drop. For this reason, throttles are often found in refrigeration applications. A typical throttling process is shown schematically in the figure below



Schematic diagram of throttle valve

The control volume of the throttle is defined by the control surfaces at 1 and 2, and the pipe-work of the system. The flow through the throttle valve can be considered to be steady and hence, for each kg of mass flowing through the system, we have the equation

$$q - w_s = (h_2 - h_1) + \frac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1)$$

There is no shaft work done in the throttle, and hence $w_s = 0$. It can be assumed that the heat losses (or gains) to the fluid passing through the throttle are negligible compared to the energy contained in the fluid itself, giving q = 0. Also, the change of potential energy of the flow passing through the throttle is small compared to the changes in the other properties, which allows us to simplify the steady flow energy equation to

$$h_2 + \frac{v_2^2}{2} = h_1 + \frac{v_1^2}{2} = h_0 = \text{const.}$$

The term $h_0 = h + \frac{v^2}{2}$ is called the *stagnation (or total) enthalpy* of the fluid; it is the enthalpy achieved in bringing the fluid to rest adiabatically.

In many cases the velocity of the fluid does not change significantly across the throttle, and the steady flow energy equation further simplifies to

 $h_2 = h_1$

The two property rule implies h(T,p) or equivalently T(h,p), which generally infers $T_2(h_2, p_2) \neq T_1(h_1, p_1)$ since $h_2 = h_1$ and $p_2 \neq p_1$.

Hence:

If the change in velocities across a throttle valve is not negligible, then the stagnation enthalpy across the valve is constant.

If the change in flow velocities across the valve is negligible, then the static enthalpy is conserved.

Example Question:

Steam flows through a throttle valve. The pressure upstream of the valve is 5 bar and the fluid is dry saturated. If the pressure drop across the valve is 4 bar, calculate the temperature of the steam downstream of the valve. The effects of velocity may be neglected.



Solution:

At state 1:
$$p_1 = 5 \text{ bar};$$
 $x_1 = 1.0$ $h_1 = 2749 \text{kJ}/\text{kg};$ $t_s = 151.8^{\circ}\text{C}$ At state 2: $p_2 = 1\text{bar}$ $h_{g2} = 2676 \text{kJ}/\text{kg};$ $t_s = 99.6^{\circ}\text{C}$

For a throttle, neglecting kinetic energy terms, $h_2 = h_1$.

It is apparent (since $h_1 > h_{g2}$) that in this problem, the steam is going to enter the superheat region. Hence, it is necessary to evaluate the temperature of superheated steam at a pressure of 1 bar which has an enthalpy of 2749kJ/kg. The values from the tables are

t (°C)	h (kJ/kg)
100	2676
150	2777

Hence the value of temperature lies between 100°C and 150°C at 1 bar. If it is assumed that the enthalpy varies linearly with temperature along an isobar then, by similar triangles

$$\frac{t-100}{150-100} = \frac{h-h_{g,100}}{h_{g,150}-h_{g,100}} = \frac{2749-2676}{2777-2676}$$

which can be rearranged to give

$$t = 100 + \frac{2749 - 2676}{2777 - 2676} \times (150 - 100) = 136.1^{\circ}C$$

5) Nozzles

The purpose of a nozzle is to convert the energy stored in the fluid (in the form of pressure) into gas velocity. Typical examples of the use of nozzles in engineering equipment are the propelling nozzles used in jet engines, and the nozzles used in steam and gas turbines to produce the flow through the blades. Nozzles can take a number of forms, but all are characterised by a change in flow area. A typical nozzle is depicted in the figure below. This is sometimes referred to as a *convergent-divergent nozzle* and sometimes called a *venturi nozzle*. The different names relate to the operating conditions.



(or venturi nozzle)

The gas flowing through the nozzle does so by virtue of a pressure difference between the entry and exit, so in this respect the nozzle is similar to the throttle. The difference between the devices is that the purpose of the throttle is to produce a pressure drop without converting the 'pressure' energy of the fluid into velocity. The example of an orifice plate mentioned earlier shows the difference between a nozzle and a throttle in terms of their **flow streamlines**.



Flow through devices in a pipe (a) orifice plate; (b) venturi nozzle

It can be seen from this sketch that the flow entering the nozzle (sketch (b)) is streamlined. There are no rapid changes in the flow profile, the flow will not **separate** and will not become turbulent. This flow will pass through the nozzle with minimal losses. On passing through the orifice plate however, the flow is not constrained downstream by a solid boundary and consequently attempts to fill the pipe. This results **in flow separation** downstream of the orifice plate, and a great deal of *turbulence* is established. This turbulence is irreversible, and causes losses in the usable energy in the flow - energy is converted from kinetic energy into thermal energy by viscous processes.

CHAPTER 5 - OPEN SYSTEMS AND ENERGY TRANSFER

The nozzle could be considered to be *adiabatic*, i.e. there are no heat losses, and for each kg of mass passing through the device, q = 0. If the steady flow energy equation is applied then

$$q - w_s = (h_e - h_i) + \frac{1}{2}(v_e^2 - v_i^2) + g(z_e - z_i)$$

It is also obvious that the work term here is zero, and this means that the steady flow energy equation can be simplified to

$$h_{e} - h_{i} = -\frac{1}{2} (v_{e}^{2} - v_{i}^{2})$$

In many cases, the flow upstream of the nozzle is from a reservoir, and hence is at the stagnation condition and $v_i = 0$. Then, the previous equation further simplifies to

$$v_{e} = \sqrt{2(h_{i} - h_{e})}$$

Example Question:

Steam, at a static pressure and temperature of 100 bar and 600°C respectively, flows down a pipe at a velocity of 100 m/s. It is then expanded in a nozzle down to exit conditions of 6 bar and 200°C. Calculate the velocity of the steam at the exit to the nozzle.

Solution:

Starting from our simplified form of the steady flow energy equation (It should always be derived from first principles with explicit assumptions!)

$$h_{e} - h_{i} = -\frac{1}{2} (v_{e}^{2} - v_{i}^{2})$$

can be rearranged to give

$$v_{e} = \sqrt{2\left\{\left(h_{i} - h_{e}\right) + \frac{v_{i}^{2}}{2}\right\}}$$

The enthalpies at entry and exit to the nozzle can be evaluated from the tables (pages 8 and 7), giving

$$h_i = 3624 \text{ kJ/kg}$$

$$h_e = 2851 \text{ kJ} / \text{kg}$$

and substituting these values into the above equation gives

$$v_e = \sqrt{2\left\{ \left(3624 - 2851\right) \times 10^3 + \frac{100^2}{2} \right\}} = 1247.4 \text{ m/s}$$

It is obvious from the values of h_i and h_e that the static enthalpy is not the same upstream and downstream of the nozzle. However, the stagnation (total) enthalpies should be the same, and this can be proven below:

$$h_{01} = h_1 + \frac{v_1^2}{2} = 3624 + \frac{100^2}{2 \times 10^3} = 3624 + 5 = 3629 \text{ kJ/kg}$$

$$h_{02} = h_2 + \frac{v_2^2}{2} = 2851 + \frac{1247.4^2}{2 \times 10^3} = 2851 + 778.0 = 3629 \text{ kJ/kg}$$

6) Heat Exchangers

A heat exchanger is a device that allows heat from a fluid (a liquid or a gas) to pass to a second fluid without the two fluids having to mix together or come into direct contact. Heat exchangers can be found alongside devices that require cooling e.g. engines, circuit boards etc. They appear in refrigerators, heat pumps, ventilation units and all manner of power devices. The schematic sketch shows a heat exchanger positioned within a control volume (CV), where the two fluids involved are distinguished by the superscripts f_1 and f_2 .



The SFEE is applicable and for this case reduces to $\int e^h d\dot{m} = 0$, which in its simplest form provides

$$\dot{m}^{f} \left(\dot{n}_{out} - \dot{n}_{m} \right) = 0$$

arising because there is no shaft work and it is reasonable to assume negligible heat loss to the surroundings.

The heat-exchange process can be visualised as consisting of two parts as depicted:



Note however that heat energy is exchanged, so $\dot{Q}_2 = -\dot{Q}_1$ and addition of the two equations for each CV returns the equation for the whole heat exchanger.

Conservation of properties across devices

The specific enthalpies at the inlet and outlet of a device are required in order to apply the SFEE. The two-property rule applies but we are often faced with insufficient information at the outlet of a device to determine the specific enthalpy. The following table lists the common assumptions made for the devices considered thus far:

Device	Assumption	Property conserved	Identity
Turbine	Reversible and Adiabatic	Entropy	$s_2 = s_1$
Compressor	Reversible and Adiabatic	Entropy	$s_2 = s_1$
Pump	Incompressible Liquid	Energy and Volume	$u_2 = u_1, v_2 = v_1$
Nozzle	Reversible and Adiabatic	Entropy	$s_2 = s_1$
Throttle	Irreversible and Adiabatic	Enthalpy	$h_2 = h_1$
Heat Exchanger	Negligible Pressure Drop	Pressure	$p_2 = p_1$

A lot more will be said about entropy and reversibility but for now view entropy as another property that can be determined.

With knowledge of any two independent properties for a particular state the rest can be determined (twoproperty rule). Thus, for the device depicted below, with two independent properties at state 1 known, then all the other properties at that state can be obtained. However, it is possible that only one property is known at state 2 and to fully define the state another independent property is needed. This is where knowledge of the property conserved comes into play (see table) allowing a second property to be determined at state 2 and fully defining the state.



Tutorial Questions

- 1. In a steam turbine the flow rate is 5000 kg/hr and the power output is 500 kW. If the heat loss from the casing is negligible, find
 - (a) the change in specific enthalpy if the velocities and elevation are the same at entry and exit;
 - (b) the change in specific enthalpy if the entry velocity is 100 m/s, the exit velocity is 400 m/s and the inlet pipe is 10 m above the exhaust.

[-360kJ/kg, -435kJ/kg]

- 2. In a certain process in industry, it is necessary to compress 500 kg of steam per hour from an initial state of 1.5 bar, 111°C with x=1 to 5.5 bar. The temperature after compression is 260° C. The heat transfer from the compressor is 10000 kJ/hr. If kinetic and potential energy changes may be neglected determine the power requirement in kW. [42.7kW]
- 3. Steam enters the nozzle of a turbine with a low velocity and at 30 bar, 350° C and leaves at 20 bar with a velocity of 510 m/s. The rate of steam flow is 5000 kg/hr. Calculate the quality of the steam leaving the nozzle and the exit area. [superheated, 284.3° C, $3.30 \times 10^{-4} m^2$]
- 4. Construction of a 1500m tall skyscraper specifies that steam heating be supplied. Assume that the steam is supplied to the top of the building by a vertical pipe. If the steam enters at the ground level as dry saturated vapour at 3 bar and transfers 100 kJ/kg in its passage to the top floor where its pressure is l bar, find the quality of the steam at this point. [0.97]
- A steady flow of steam enters a condenser with a specific enthalpy of 2000 kJ/kg and a velocity of 500 m/s. The condensate leaves the condenser with an enthalpy of 100 kJ/kg and a velocity of 10 m/s. If the steam flow rate is 50 kg/s. and the cooling water temperature rise is limited to 30°C, determine the cooling water flow rate. [806.2kg/s]
- 6. A steady flow of steam at 7 bar and 200°C enters a device. It leaves at the same level and velocity but the pressure has increased to 15 bar. A shaft projecting into the device supplies 500 kJ of work per kg, of steam and 700 kJ/kg of steam are lost from the device. Find the temperature and condition of the steam leaving the device. [$x_2=0.93$]
- 7. 1 kg of steam at 7 bar and 200°C is contained in a cylinder. It compressed until the pressure becomes 15 bar. The work done on the piston is 500 kJ and the heat loss is 700 kJ. Find the final temperature and condition. $[x_2=0.91]$
- 8. Liquid ammonia at a temperature of 40°C and a pressure of 20 bar is mixed in a steady flow process with saturated vapour at 20 bar. The mass flow of liquid and vapour are equal and after mixing the pressure is 18.30 bar and the quality 0.85. Calculate the heat transfer per unit mass of mixture [390.3 kJ/kg(mix)]

CHAPTER 6

WORKING FLUID: GASES

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OTHER EQUATIONS OF STATE	Page 6.14
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Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 4 "Energy Analysis of Closed Systems" pages 174-187.

Introduction

This section is principally concerned with ideal gases and in particular the equation of state that relates pressure, volume and temperature for a fixed mass of gas in a state of thermodynamic equilibrium. The equation of state (or state equation) takes on a number of equivalent forms. The founding principle that underpins the various relationships is Avogadro's hypothesis, which states that *equal volumes of gas at equal pressures and temperatures contain the same number of molecules*. A consequence of this hypothesis is that the equation of state can apply to many gases and one form of the state equation is

pV = NkT

where k is Boltzmann's constant and equals 1.38065×10^{-23} J/K and N is the number of molecules.

This form of the equation provides a link between the microscopic and the macroscopic but is not in a form ideal for use by engineers since it involves both large and tiny numbers. An alternative form used by chemists (arising from Avogadro's hypothesis) uses moles (the amount of substance) rather than N where 1 mole contains the same number of particles as there are in 12g of carbon-12 (¹²C) atoms, which equals 6.022×10^{23} (know as Avogadro's number) and is the numerical value of Avogadro's constant $N_{A} = 6.022 \times 10^{23} \text{ mol}^{-1}$.

The number of moles n (units of mol) for an arbitrary gas is simply $n = N/N_A$ and on replacing N in pV = NkT a more convenient equation of state is obtained, i.e.

$$pV = n(N_Ak)T = n\Re T$$
,

where \Re is the universal gas constant and equals $\Re = 8.3145 \text{ J/mol K}$ (or $\Re = 8.3145 \text{ kJ/kmol K}$)

Although this form is convenient as it now contains manageable numbers it is sometimes advantageous to utilise mass m rather than mole n. This can be achieved on definition of the **molecular weight** (now more correctly called the **relative molecular mass**) which is a dimensionless quantity equal to the ratio of the mass of a molecule and one twelfth the mass of a carbon-12 atom. A quantity having the same numerical value as the molecular weight for 1 mole of substance is the **molar mass** M (some books confusingly refer to this as molecular weight) measured in g/mol (or kg/kmol).

It follows that n = m/M, which can be substituted into $pV = n\Re T$ to give

$$pV = m(\Re/M)T = mRT$$
,

where R is the **characteristic gas constant** for the gas under consideration and is measured in units J/gK (or more conveniently kJ/kgK). Dividing the equation of state through by m gives a particularly convenient form

$$pv = RT$$

and similarly dividing by V gives

 $p = \rho RT$.

Note that the equation of state for an ideal gas satisfies the two properly rule since for example p(V,T).

A rather interesting question arises, which is: might the gas law (equation of state) inform us about the behaviour of other state functions such as internal energy U (or u) or enthalpy H (or h)? It transpires that it is possible to show that both U and H for a closed system of ideal gas at equilibrium are solely functions of temperature, i.e. U(T) and H(T). A formal proof of this is left until entropy is introduced but let us first examine some experimental evidence that supports the contention.

Historical developments

Boyle's Law

In 1662, soon after it became possible to pump gases, Robert Boyle discovered an approximate relationship between the pressure of a gas and its specific volume. This relation held true when the temperature was maintained constant. Boyle found that pv = constant for temperature t = constant. This implied that pv = f(t), however the relationship only applied to permanent gases, i.e. gases that existed at the ambient conditions of the experiment. Today we interpret that to mean fluids that are in a superheated state at 'ambient' conditions.

Joule's (second) Law

In 1845, Joule carried out an experiment whose arrangement is shown below



In the experiment, the left hand container contains gas, while the right hand vessel is completely evacuated. A valve separates the two vessels, and the entire apparatus is immersed in a water bath. The valve is suddenly opened, and gas flows from vessel 1 to vessel 2. As the gas is undergoing an unresisted expansion, the amount of work it does is zero. Joule found that the temperature of the water bath did not change during the experiment, indicating that the net heat transfer during the process was zero. From the first law

$$U_2 - U_1 = Q_{1-2} - W_{1-2}$$
.

Now, knowing that both the pressure and the specific volume varied significantly during the experiment, Joule was able to conclude

U = U(t) (to experimental accuracy)

The total intrinsic internal energy for an ideal gas is a function of *temperature* alone. Since U = mu, and $m \neq m(t)$, it follows that u = u(t), i.e. the specific intrinsic internal energy for an ideal gas is a function of temperature alone.

One has to be a little bit careful here because the specific heat for the water is relatively large ($\approx 4.18 \text{ kJ/kgK}$), so temperature rise could typically be small for a sufficiently large mass of water and therefore possibly not picked up by the thermometer used.

Analysis of Joule's Experiment

The first law applied to the Joules experimental apparatus gives (in specific quantities)

$$du = \delta q - \delta w$$

but no heat transfer is observed, and the net work done is zero, (as there is a vacuum in container B). These two observations lead to

du = 0

CHAPTER 6: GASES

Now recall from earlier lectures that any equilibrium thermodynamic state can be found using the two property rule. This means that the internal energy can be written u = u(T,p) or u = u(T,v), where T is the (as yet not formally defined) *absolute* temperature. Expanding the internal energy differential gives

$$du = \left(\frac{\partial u}{\partial T}\right)_{p} dT + \left(\frac{\partial u}{\partial p}\right)_{T} dp$$
$$du = \left(\frac{\partial u}{\partial T}\right)_{v} dT + \left(\frac{\partial u}{\partial v}\right)_{T} dv$$

Joule found that during the experiment, the change in water bath temperature was zero, and hence dT = 0. During the experiment, both specific volume and pressure changed significantly, implying $dp \neq 0$, $dv \neq 0$. This leads to the conclusion that, for an ideal gas

$$du = \left(\frac{\partial u}{\partial p}\right)_{T} dp = 0 \iff \left(\frac{\partial u}{\partial p}\right)_{T} = 0 \iff u = u(T)$$
$$du = \left(\frac{\partial u}{\partial v}\right)_{T} dv = 0 \iff \left(\frac{\partial u}{\partial v}\right)_{T} = 0 \iff u = u(T)$$

The Joule-Thomson experiment

In 1852, Joule and Thomson (later Lord Kelvin), devised a steady flow experiment in order to demonstrate that the *enthalpy* of an ideal gas was a function of temperature alone. The experimental arrangement is shown in the figure below.



A porous plug is placed in a pipe. High pressure gas is driven through the pipe and across the porous plug. In flowing through the plug, the pressure of the gas is reduced significantly. The pipe is insulated, is arranged horizontally and the flow through it has negligible kinetic energy. Recalling that the steady flow energy equation per unit mass passing through the systems is

$$q - w_s = \left(h + \frac{v^2}{2} + gz\right)_e - \left(h + \frac{v^2}{2} + gz\right)_i$$

which reduces to

 $h_e = h_i$

i.e. the enthalpy upstream of the plug is the same as that downstream. During their experiments, Joule and Thomson measured the temperature upstream and downstream of the porous plug. They found that the temperature change across the plug was negligible. As the pressure and specific volume varied significantly between the inlet and the outlet of the system, they were able to conclude

$$h = h(t)$$
 alone

i.e. the enthalpy of an ideal gas is a function of the temperature alone. The argument behind this statement is exactly analogous to that presented for the internal energy.

Observation

It is worth pointing out in passing that $h_e = h_i$ with h = h(t) implies that $t_i = t_e$, so unlike vapours (and real gases) throttling an ideal gas flow has no impact on the gas temperature. Note also that Boyle's law has shown that (at least approximately) pv = f(t), and Joules original experiment found internal energy to be a function of temperature alone (again, approximately) hence h = u + pv = h(t).

Equation of State of an Ideal Gas

The discoveries of Boyle, Joule and Thomson can be embodied in a single equation, the ideal gas equation of state

$$\frac{pv}{T} = constant = R$$

The constant appearing in the Ideal Gas Law is called **the characteristic gas constant**, and is usually denoted by R. It is called a characteristic gas constant because it varies from gas to gas. The units for R

are J/kgK since
$$[R] = \left[\frac{pv}{T}\right] = \left[\frac{N}{m^2}\right] \times \left[\frac{m^3}{kg}\right] \times \left[\frac{1}{K}\right] = \left[\frac{Nm}{kgK}\right] = \left[\frac{J}{kgK}\right].$$

Specific Heats for Ideal and Perfect gases

An ideal (and perfect) gas satisfies the relationship u = u(T) but recall the definition of specific heats c_v and c_p , i.e.

$$\mathbf{c}_{v} = \left(\frac{\partial \mathbf{u}}{\partial T}\right)_{v} \quad \mathbf{c}_{p} = \left(\frac{\partial \mathbf{h}}{\partial T}\right)_{p}.$$

so it immediately follows that $c_v = \frac{du}{dT}$ and $c_p = \frac{dh}{dT}$, i.e. partial derivatives collapse to ordinary differentiation.

Despite this these relationships they tell us nothing about the specific behaviour of the specific heats but evidently for an ideal gas $c_v = c_v(T)$ and $c_p = c_p(T)$.

In the case of a **perfect gas** (by **definition**) the behaviour of the specific heats is rather simple and is restricted to that subset of gases for which: $c_v = const$ and $c_p = const$.

Ideal Gases in Closed and Open Systems

For closed systems, the first law is written

$$du = \left(\frac{\partial u}{\partial T}\right)_{v} dT + \left(\frac{\partial u}{\partial v}\right)_{T} dv = c_{v} dT = \delta q - \delta w$$

since $\left(\frac{\partial u}{\partial T}\right)_{u} = c_{v}$ and $\left(\frac{\partial u}{\partial v}\right)_{T} = 0$ arising because u = u(T), where it is assumed here that the

substance is not undergoing a change of phase.

Integration gives

$$\int_{u_1}^{u_2} du = u_2 - u_1 = \int_{T_1}^{T_2} c_v(T) dT = q_{1-2} - w_{1-2}$$

More generally, internal energy of an ideal gas at a given temperature T is defined as

$$u(T) = \int_{T_o}^{T} c_v(T) dT + u_0$$

where \mathbf{u}_0 is a reference internal energy defined at a temperature \mathbf{T}_0 .

As the reference temperature is arbitrary, so too is the absolute value of the internal energy u_0 . This emphasises the fact that thermodynamics is interested in the **change** of state of a system (for which, reference values cancel out).

Returning to the First Law for closed systems and ideal gases $c_v dT = \delta q - \delta w$ where the system of interest comprises of a piston in a cylinder, which is allowed to move in order to maintain constant pressure



$$p = \text{constant}$$

$$\delta q = c_v dT + \delta w$$

$$\delta q = du + pdv$$

$$= d(u) + d(pv) = d(u + pv) = dh$$

$$= c_v dT + d(pv)$$

$$= c dT + RdT$$

Thus it follows that $\delta q = dh = (c_v + R)dT$ and on writing h as a differential in terms of two properties

$$dh = \left(\frac{\partial h}{\partial T}\right)_{p} dT + \left(\frac{\partial h}{\partial p}\right)_{T} dp = c_{p} dT$$

since
$$\left(\frac{\partial h}{\partial T}\right)_{p} = \frac{dh}{dT} = c_{p}$$
 and $\left(\frac{\partial h}{\partial p}\right)_{T} = 0$. By comparison,

 $dh = (c_v + R) dT$, from which we conclude that, for an ideal gas that

$$c_n = c_v + R$$

or

$$R = c_p - c_v$$

In general

$$u = u(T) \quad c_v = c_v(T) = \frac{du}{dT}$$
$$h = h(T) \quad c_p = c_p(T) = \frac{dh}{dT}$$

it follows that

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$$\mathbf{R} = \mathbf{c}_{p}(\mathbf{T}) - \mathbf{c}_{v}(\mathbf{T})$$

Similar to internal energy enthalpy is defined as

$$h(T) = \int_{T_0}^{T} c_p(T) dT + h_0$$

where $h_0 = h(T_0)$ is a reference enthalpy taken at an arbitrary reference temperature.

Open systems (steady state)

In an open system, the First Law in differential form is

$$de^{h} = dh + vdv + gdz = \delta q - \delta w_{s}$$
.

This can be written as

$$c_p dT + v dv + g dz = \delta q - \delta w_s$$

or, in integrated form

$$\int_{T_1}^{T_2} c_p(T) dT + \left(\frac{v_2^2 - v_1^2}{2}\right) + g(z_2 - z_1) = q_{1-2} - (w_s)_{1-2}.$$

Work done on a Polytropic Process

While not strictly part of the gas laws, it is useful to examine the work done during polytropic processes when the working fluid is an ideal gas. Recall in the lectures on work that engineering processes could often be written in the form

 $pv^n = const.$

The process $pv^n = const$ was referred to as a *polytropic* process, with *n* defined as the polytropic index. Recall that:

1.
$$n = 0$$
 $w_{1-2} = \int p dv = p(v_2 - v_1)$
2. $n \neq 1$ $w_{1-2} = \frac{p_1 v_1 - p_2 v_2}{n-1}$

3.
$$n=1$$
 $\mathbf{w}_{1-2} = \mathbf{p}_1 \mathbf{v}_1 \ln\left(\frac{\mathbf{v}_2}{\mathbf{v}_1}\right) = \mathbf{p}_2 \mathbf{v}_2 \ln\left(\frac{\mathbf{v}_2}{\mathbf{v}_1}\right).$

Using the gas laws, these may be re-written as

1.
$$n = 0$$
 $w_{1-2} = R(T_2 - T_1)$
2. $n \neq 1$ $w_{1-2} = \frac{R(T_1 - T_2)}{n-1}$

$$w_{1-2} = RT_1 \ln\left(\frac{v_2}{v_1}\right) = RT_2 \ln\left(\frac{v_2}{v_1}\right)$$
$$= RT_1 \ln\left(\frac{p_1}{p_2}\right) = RT_2 \ln\left(\frac{p_1}{p_2}\right)$$

Alternative forms for polytropic processes

3.

Up until this point, polytropic processes have been written in the form $pv^n = const$. However, this is not the only way of describing a polytropic process. Indeed, equivalent equations relating any two of the three primitive variables p, T, or v can be used. For example given $pv^n = const$ and pv = RT, then

$$p\left(\frac{RT}{p}\right)^n = \text{const}$$

gives

 $p^{1-n}T^n = \frac{T^n}{p^{n-1}} = \text{const.}$

$$\left(\frac{RT}{v}\right)v^n = const.$$

 $Tv^{n-1} = const$

gives

Similarly

In conclusion

$$pv^{n} = const$$
$$\frac{T^{n}}{p^{n-1}} = const$$
$$Tv^{n-1} = const$$

are **mathematically identical** ways of saying the same thing for an ideal gas, i.e. each of these equations describes (for the **same** value of *n*), the **same** polytropic process.

Example Question:

5 kg of gas, initially at 298 K and a pressure of 1 bar is heated to 600K and 6 bar. Calculate

- 1. The work done.
- 2. The change in internal energy.
- 3. The total heat transferred.

Assume that the process undergone by the gas is polytropic, and that gas can be treated as ideal. R = 287 J/kgK; $c_p = R (3.3 + 0.00141\text{ T})\text{J/kgK}$.

Solution:

The process is polytropic but the polytropic index is unknown.

Step 1: find the polytropic index

Given p_1, T_1 and p_2, T_2 and that the process is polytropic, it follows that $p_1^{1-n} T_1^n = p_2^{1-n} T_2^n$ or

$$\left(\frac{\mathbf{p}_2}{\mathbf{p}_1}\right) = \left(\frac{\mathbf{T}_2}{\mathbf{T}_1}\right)^{\left(\frac{\mathbf{n}}{\mathbf{n}-\mathbf{y}}\right)}$$

solving for *n*;

$$n = \frac{\ln\left(\frac{p_1}{p_2}\right)}{\ln\left(\frac{p_1T_2}{p_2T_1}\right)} = \frac{\ln\left(\frac{1}{6}\right)}{\ln\left(\frac{1\times600}{6\times298}\right)} = 1.641$$

Step 2: find the work done

Now, we know that n > 1, and so the specific work w_{1-2} is

$$w_{1-2} = \frac{R}{n-1} (T_1 - T_2) = \frac{287}{0.641} (298 - 600) = -135.2 \frac{kJ}{kg}$$

and the total work W_{1-2} is

$$W_{1-2} = mw_{1-2} = 5 \times \left(-135.2 \frac{kJ}{kg}\right) = -676.1 kJ$$

Step 3: find the change in internal energy

$$u_{2} - u_{1} = \int_{T_{1}}^{T_{2}} c_{v}(T')dT' = \int_{T_{1}}^{T_{2}} (c_{p}(T') - R)dT$$

$$= \int_{T_{1}}^{T_{2}} c_{p}(T')dT' - R(T_{2} - T_{1})$$

$$= \int_{T_{1}}^{T_{2}} R(3.3 + 0.00141T)dT - R(T_{2} - T_{1})$$

$$= R\left\{ \left[3.3T + \frac{0.00141T^{2}}{2} \right]_{T_{1}}^{T_{2}} - (T_{2} - T_{1}) \right]$$

$$= R\left\{ 2233.8 - 1046 - (600 - 298) \right\}$$

$$= 254.22 \frac{kJ}{kg}$$

$$U_{2} - U_{1} = 1.271MJ$$

Step 4: find the total heat transferred

$$Q_{1-2} - W_{1-2} = U_2 - U_1$$
$$Q_{1-2} = 1.271 \times 10^6 + (-676.1 \times 10^3)$$
$$= 595.1 \text{kJ}$$

Perfect Gases

An ideal and a perfect gas is one, which obeys the relations $\frac{pv}{T} = \text{const}$, u = u(T) and h = h(T) and in the case of a polytropic process each satisfies $pv^n = \text{const}$, $p^{1-n}T^n = \text{const}$ and $Tv^{n-1} = \text{const}$. In the case of a perfect gas however $c_p = \frac{dh}{dT} = \text{const}$ and $c_v = \frac{du}{dT} = \text{const}$, which immediately infers that h and u are linear functions of T, i.e.

$$h(T) = c_{p} \int_{T_{0}}^{T} dT' + h_{0} = h_{0} + c_{p} (T - T_{0})$$
$$u(T) = c_{v} \int_{T_{0}}^{T} dT' + u_{0} = u_{0} + c_{v} (T - T_{0})$$

Alternative forms for the equation of state

Up to now, an ideal or perfect gas has been one which obeys pv = RT where $p = pressure (N/m^2)$, $v = specific volume (m^3/kg)$, R = characteristic gas constant (J/kgK) and T = temperature (K).

An alternative form is obtained by multiplying both sides of the equation with mass;

p(mv) = mRTpV = mRT

where V is now the **total** volume of the system, and has units of m^3 .

A third way is to take the specific volume appearing in pv = RT and move it to the right hand side of the equation

$$p = \frac{RT}{v} = \rho RT$$

since $v^{-1} = \rho$, where ρ is the **density** of the gas, and has units of kg/m³.

The molar form for the equation of state

All of the above gas laws have been based on the mass of the system (i.e. defined in terms of kg). In many applications (such as combustion), using the mass of a particular gas may not be as appropriate as using the **molar mass** of the gas. As a demonstration, consider the following chemical reaction

$$CH_4 + H \rightarrow CH_3 + H_2$$

In words, the above equation means "during a chemical reaction, 1 unit amount of CH_4 (methane) and 1 unit amount of H are converted to 1 unit amount of CH_3 and one unit amount of H_2 (hydrogen)". Let us now examine what is meant by *unit amount*.

Avogadro's Hypothesis

In 1811, Avogadro put forward the proposition that "equal volumes of gas at equal pressures and temperatures contain the same number of molecules".



In this sketch, $V_1 = V_2$, and the pressures and temperatures in both containers are equal. Under these circumstances, Avogadro's hypothesis says something about the **numbers** of molecules in each container, but not their masses. The examples of H₂ and CO₂ were picked because carbon dioxide is much heavier than elemental hydrogen. The box containing the H₂ on the left will (providing p, V and T are the same in both containers) be 22 times less massive than the box containing CO₂ on the right hand side.

Rather than think on terms of mass, Avogadro thought in terms of numbers of molecules. He proposed the idea of a *mole* of substance. Referring back to the above example, Avogadro said that both containers contain the same numbers of **moles** of gas. The chemists refer to this quantity as the *amount-of-substance*.

How much is a mole of gas?

• A mole of gas contains N_A molecules, where N_A is Avagadro's constant.

$$N_{A} = 6.022045 \times 10^{23} \text{ mol}^{-1}$$
$$= 6.022045 \times 10^{26} \text{ kmol}^{-1}$$

How do we relate a mole of gas to its mass?

To answer this, it is necessary to define the **molecular** weight. The molecular weight M_w of a substance is defined as the dimensionless quantity

 $M_w = \frac{Mass of one molecule of substance}{(1/12) mass of one atom of carbon - 12}$

A quantity having the same numerical value as $M_{\rm w}$ for 1 mole of substance is the **molar mass** M measured in g/mol (or kg/kmol). To convert the molar mass M of a gas to its associated mass, is simply related by

m = Mn

where n is the number of moles.

Some molar masses for common gases/elements are given below.

Gas/Element	M(kg/kmol)
H ₂	2
O_2	32
N_2	28
СО	28
CO ₂	44
H ₂ O	18
С	12

Example Question: Find the mass of 6 kmol of O₂

Solution:

Example Question: If a system contains 1.8kg of CH₃OH, find the associated molar mass.

Solution: Firstly, we need to find the molecular weight of CH_3OH . To do this, we sum the molecular weights of its constituent components

$$(M_w)_{CH_{3}OH} = (1 \times 12) + (3 \times 1) + (1 \times 16) + (1 \times 1) = 32$$

 $m = Mn = 32 \times 6 = 192 kg$

Now, m = 1.8 kg and so

$$\frac{m}{M} = n = \frac{1.8}{32} = 0.05625$$
 kmol.

The universal gas constant and the ideal (molar) gas law

Substitution of m = Mn into pV = mRT gives

$$pV = nMRT$$

Now, consider our containers filled with H₂ and CO₂.



Each container has the same volume, and is filled to the same pressure and temperature.

$$\frac{p V}{T} = (M R)_{H_2} n_{H_2}$$
$$\frac{p V}{T} = (M R)_{CO_2} n_{CO_2}$$

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Since pressure, temperature and volume are the same in both containers, it follows that the number of molecules (Avogadro's hypothesis) and hence the number of moles (since is $n = \frac{N}{N_A}$) is the same i.e.

$$\mathbf{n}_{\mathrm{H}_2} = \mathbf{n}_{\mathrm{CO}_2}$$

and form the ideal gas equation of state reduces provides

(

$$\left(\mathrm{MR}\right)_{\mathrm{H}_{2}} = \left(\mathrm{MR}\right)_{\mathrm{CO}_{2}}$$

irrespective of the gases used, the combination MR always provides the same constant. This constant is termed the **universal gas constant** (universal because it applies to *all* gases) and is defined

$$(MR)_{H_2} = (MR)_{CO_2} = \Re = 8314.5 \frac{J}{kmolK}$$

The definition above provides a method for calculating the *characteristic* gas constant for any gas.

Example Question: Find the characteristic gas constant for methane (CH₄).

Solution:

$$(M_w)_{CH_4} = (1 \times 12) + (4 \times 1) = 16$$

 $R_{CH_4} = \frac{\Re}{M_{CH_4}} = \frac{8314.5}{16} = 519.7 \text{J/kgK}$

The ratio of specific heats

In many applications, the ratio of the specific heats plays an important part and it is useful to define

$$\gamma = \frac{c_p}{c_v}$$

One of the most important processes encountered in the course is an **isentropic** process (constant entropy). For ideal gases, an isentropic process can be described by equations that look similar to the polytropic processes. The difference between polytropic and isentropic processes is that the polytropic index $n = \gamma$, i.e. an isentropic process is defined by the following equations

$$pv^{\gamma} = const$$

 $p^{1-\gamma}T^{\gamma} = const$
 $Tv^{\gamma-1} = const$

What is *meant* by an isentropic process is considered later in the course.

Other Equations of State (for information only)

The ideal gas equation of state can be derived by purely analytic means from statistical mechanics. The derivation is beyond the scope of this course (and, indeed most undergraduate courses), but it does highlight what assumptions are implicit in a gas which behaves ideally. These assumptions are found to be:

- (i) The molecules are perfectly rigid, elastic spheres.
- (ii) The volume occupied by the molecules is negligible compared to the total volume.
- (iii) There are no forces of attraction between molecules.

The last two assumptions become decreasingly accurate if the gas occupies a region close to the saturated vapour lines



Assumption (ii) holds well in the low density limit. As $\rho = p/RT$, this implies that gases behave ideally at low pressure and high temperature.

As the pressure increases and the temperature drops, the volume occupied by the molecules must be accounted for. This is done in the **Clausius equation of State**,

$$p = \frac{RT}{v - b}$$

where *b* is the volume occupied by the molecules.

As the molecules approach one another, the assumption of negligible attraction becomes questionable. An attempt to accommodate molecular forces levels to **the Van der Waals' equation of state**,

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

where the last term tries to accommodate the forces of attraction and is equivalent to an inverse square law. There are many other equations of state, most notably the **virial equation**

$$pv = RT\left(1 + \frac{b}{v} + \frac{c}{v^2} + \dots\right)$$

and the Beattie-Bridgeman equation

$$p = \frac{RT}{v^2} \left(1 - \frac{c}{vT^3} \right) \left(v + B_o \left(1 - \frac{b}{v} \right) \right) - \frac{1}{v^2} A_o \left(1 - \frac{a}{v} \right)$$

where a, b, c, A_o and B_o are constants appropriate to the particular gas.

Gas mixtures

The analysis thus far as been limited to single-component gas systems but it transpires (as a consequence of Avogadro's principle) non-reacting gas mixtures such as air can behave like an ideal gas. The difficulty with applying the equation of state pv = RT is that the characteristic gas constant is required for the mixture. However, R is still obtainable from the relationship $R = \Re/M$, but in this case M is the **mean** molar mass defined to be M = m/n.

Consider a two component gas system with $n = n_1 + n_2$, where n_i is the number of moles of gas component i. Similarly $m = m_1 + m_2$ where m_i is the mass of gas component i. Note that the molar masses for each component are $M_i = m_i / n_i$. It follows that

$$M = \frac{m}{n} = \frac{m_1 + m_2}{n} = \frac{n_1 M_1 + n_2 m_2}{n} = \left(\frac{n_1}{n}\right) M_1 + \left(\frac{n_2}{n}\right) M_2 = y_1 M_1 + y_2 M_2$$

where $y_i = n_i / n$ are the *mole fractions*

It can sometimes be useful to define *mass fractions* $Y_i = m_i/m$. Analysis of a mixture on the basis of mass (or weight) is termed *gravimetric analysis* whilst analysis on the basis of moles (or volume) is termed *volumetric analysis*.

Example Question: Molar analysis of air indicates that is composed primarily of nitrogen (78%) and oxygen (22%). Determine the characteristic gas constant for the mixture along with mass fractions.

Solution: In this case mole fractions are $y_1 = 0.78$ and $y_2 = 0.22$, and the molar masses are $M_1 = 28$ kg/kmol and $M_2 = 32$ kg/kmol (see table above). Thus

 $M = y_1M_1 + y_2M_2 = 0.78 \times 28 + 0.22 \times 32 = 28.88 \text{ kg/kmol}$ and recall that $\Re = 8.3145 \text{ kJ/kmol}K$, so it follows that $R = \Re/M = 8.3145/28.88 = 0.288 \text{ kJ/kgK}$. Note that

$$Y_{i} = \frac{m_{i}}{m} = \frac{n_{i}M_{i}}{m} = \frac{(n_{i}/n)M_{i}}{(m/n)} = \frac{y_{i}M_{i}}{M}$$

so gravimetric analysis reveals $Y_1 = 0.78 \times \frac{28}{28.88} = 0.756$ and $Y_2 = 0.22 \times \frac{32}{28.88} = 0.244$.

Example Question: Molar analysis of air indicates that is composed primarily of nitrogen (78.09%), oxygen (20.95%), Argon (0.93%) and Carbon dioxide (0.03%). Given that the molecular weight of Argon is 40 determine the characteristic gas constant for the mixture along with mass fractions.

Solution: Have a go at this yourself and compare your answer with the value in the steam tables on page 26.

Tutorial Questions

- 1) A gas turbine develops a power of 10,000 kW when the gas mass flow rate is 25 kg/s. The gas flows steadily into the nozzle of the turbine at a pressure of 4 bar and velocity of 150 m/s. The gas leaves the turbine at a pressure of 1.1 bar, a temperature of 482°C and velocity of 300 m/s. The expansion process may be assumed to be adiabatic. Assume the gas to be perfect and take $c_p = 1.15 \text{ kJ/kgK} \text{ and } R = 0.290 \text{ kJ/kgK}$
 - (a) Calculate (i) the temperature of the gas entering the turbine; (ii) the flow area at entry to the turbine nozzles.
 - (b) If the gas leaving the turbine flows into a cooler; and at the exit of the cooler the gas pressure is 1 bar, its temperature is 70°C and the velocity is 100 m/s, determine the heat transfer from the gas in the cooler.

[1132K, 0.137m², -513.8kJ/kg]

- 2) A cylinder contains 1.4 kg gas at 13.8 bar and 116°C. The gas expands until the pressure becomes 1.7 bar and the temperature 43°C, the expansion following a straight line on the *p v* diagram. Determine the amount of heat received by the gas during the expansion. Take R = 0.2871 kJ/kg K; $c_v = 0.718$ kJ/kg K. [417.7kJ]
- 3) Air, with a volume of 0.34 m³, at 1 bar and at 27°C is compressed to 0.028 m³ according to the law $pV^{1.3}$ = constant. Determine the work done and the heat received by the air. Take the ratio of specific heats, $\gamma = 1.4$, and the gas constant, R = 0.2871 kJ/kg K.

[-320kJ/kg,-80kJ/kg]

- 4) A mass of 0.5 kg of hydrogen at a temperature of 15°C and pressure of 14 bar expands according to the law $pV^{1.25} = c$ until the volume is four times the initial volume. Determine the work done and heat received by the hydrogen. Take $\Re = 8.314$ kJ/kmol K; $\gamma = 1.4$, and molecular weight, $M_w = 2$. [0.7MJ, 0.26MJ]
- 5) A perfect gas with a mass of 0.5 kg occupies a volume of 0.17 m³ and is allowed to expand according to the law $pV^{\gamma} = c$ until the volume is 0.425 m³. During the expansion the temperature of the gas falls to 170°C and the work done is 67 kJ. If R = 0.2871 kJ/kg K, find (a) the values of c_p and c_{ν} , and (b) the initial pressure and temperature of the gas.

[1244.1J/kgK, 957J/kgK, 583.2K, 4.92bar]

- 6) A quantity of gas is expanded from a pressure of 2 bar to 0.9 bar. The relationship between pressure and volume at any point being given by $V = \sqrt{0.29 0.14p}$ where V is in m³ and p in bar. The initial temperature is 70°C, $c_p = 1.004$ kJ/kg K and $c_v = 0.717$ kJ/kgK. Calculate the heat received by the gas during the process. [89kJ]
- 7) The expansion of a perfect gas follows the law p = aV+b, where *a* and *b* are constants. The initial and final pressures are 6.9 bar and 2 bar respectively, and the corresponding volumes are 0.1 m³ and 0.33 m³. The mass of gas is 0.7 kg; R = 0.26 kJ/kg K and $\gamma = 1.39$. Find (a) the maximum value of the specific internal energy assuming it is zero at 0°C, and (b) the net heat added during the process. [49.53kJ, 94.7kJ]

Requires Second Law Material

- 8) A gas occupies 0.11 m³ at 1.1 bar and 20°C. If the gas undergoes a reversible, adiabatic compression to 6.7 bar, determine the final temperature, volume and the change of internal energy. Take R = 0.1901 kJ/kg K; $c_v = 0.570$ kJ/kg K. [459K, 0.03 m², 91.77 kJ/kg]
- 9) A mass of 1kg of air, occupying 4m³ at 8 bar and 200°C, expands isothermally to a volume of 12 m³. Determine the change in entropy. [7.43 kJ/kgK]
- 10) A gas, initially occupying a volume of 1 m³ at 30°C and 6 bar, expands until the volume is 4 m³ according to the law $pV^{l.25} = c$. If the specific heat at constant volume, $c_v = 13.2 \text{ kJ/kg K}$ and the ratio of specific heats, $\gamma = 1.4$, determine the total change in entropy. [2.744 kJ/kgK]
- 11) Hydrogen, occupying a volume of 2000 cm³ at 1 bar and 30°C, is compressed to 17.85 bar according to the law $pV^{l.35} = c$. The gas then cools to 100°C at constant pressure after which it is expanded isothermally down to 1 bar. Calculate the change of entropy for each process and show that the sum of these changes agrees with the change calculated using the two end points only. Take $c_p = 13.53$ kJ/kg K and $c_v = 9.68$ kJ/kg K. [2812J/kgK]

CHAPTER 7

THE SECOND LAW: HEAT ENGINES

THE CHAPTER COVERS:

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Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 6 "The Second Law of thermodynamics" pages 275-311.
Introduction

Thus far from our discourse we have seen that the formularisation and interpretation of the zeroth and first laws gave rise to the thermodynamic properties temperature T and intrinsic internal energy U, respectively. Likewise the second law implies the existence of the thermodynamic property entropy (symbol S). Entropy is often considered recondite by students but at this stage can be viewed simply as a measure of the *quality* of energy in contrast to U which a measure of the *quantity* of energy. Low entropy infers high quality and conversely high entropy means low quality. Entropy is also linked with other words such as *disorder*, *spontaneous* and *reversibility*.

As with T and U a microscopic description of entropy is possible with entropy being a measure of the uncertainty in the precise energy levels molecules occupy (this is essentially what is meant by *disorder*). This notion is encapsulated quantitatively by the formula for *absolute entropy*

$$S = k \ln W$$
,

where k is Boltzmann's constant and equals 1.38065×10^{-23} J/K and W is a measure of the number of ways the molecules of a system can be arranged to achieve the same total energy (the *weight* of an arrangement). This formula does not belong to the realm of classical thermodynamics (more to do with statistical mechanics really) so is only of passing interest here. It is of interest to note (again in passing) that at absolute zero molecules are in their lowest state of energy (the ground state) and provided this state is unique (non-degenerate) then W = 1 and S = k ln 1 = 0; reflecting that fact there is no uncertainty in the distribution of energy at absolute zero. Entropy is essentially a measure of nature's proclivity for disorder as opposed to order.

The word *spontaneous* mentioned above refers to a change not needing to be driven by work. The flow of energy from a hot reservoir to a cold reservoir in the form of heat is a spontaneous change. A particular manifestation of the second law is that *the entropy of the universe (system plus surrounding) increases in the course of any spontaneous change*. Since loosely speaking the word *spontaneous* is synonymous with the word *natural* it is clear that second law in this form infers that natural processes result in the energy of substances lowering in quality (which is rather worrying!).

Another word highlighted is *reversibility* which refers to a reversible process or reversible cycle if the process is cyclic. This is a process that can be *reversed* by means of infinitesimal changes in some property of the system without dissipation of energy (entropy production). The system is in thermodynamic equilibrium throughout the entire process and since it would take an infinite amount of time for the reversible process to finish, perfectly reversible processes are impossible. The importance of reversible processes which are cyclic is that they do not involve entropy production. Moreover, the classical definition for entropy in differential form is

$$dS = \frac{\delta Q_{rev}}{T}$$

where $\,\delta Q_{_{rev}}\,$ is an increment of heat reversibly applied.

Classical thermodynamics introduces the second law via devices called *heat engines*, which operate between *thermal reservoirs*, where a thermal reservoir is a hypothetical body with an infinite heat capacity. The defining quality of a reservoir is that it can reject or absorb quantities of heat without changing temperature. A *heat engine* is a **continuously** operating thermodynamic system, across the boundaries of which only heat and work can flow, where the phrase *continuously operating* implies that the working fluid in the heat engine undergoes a **cycle**.

The Usefulness of Energy

Consider a ship on the ocean and assume that the sea temperature is uniform. The sea must contain countless Giga Joules of energy as a result of the water having a temperature above absolute zero. Is it possible however build a ship's engine that extracts heat directly from the sea, and converts that energy into shaft work to drive the ship?



Similarly consider a box containing gas. Into one side of the box is inserted a paddle wheel. Suppose now that the gas is heated. From the first law applied to the initial heating process $q = u_2 - u_1 > 0$.



- Why does the system not drive the shaft?
- Why must $w_s = 0$, even though the intrinsic internal energy of the fluid has been increased?
- Using the same box, why is it possible to convert work to heat directly, but not possible to convert heat into work directly?

Non-reversible processes

A glass of water on a table contains potential energy (as well as water!) as a result of its position on the table top. If the glass falls, potential energy is converted into kinetic, acoustic and thermal energy (from falling, shattering and bringing the moving water to rest via viscosity, respectively). The first law is satisfied by the system. The reverse would also be true, i.e. if all the liquid converts its thermal energy back into the reassembling glass, which then leaps back up onto the table, the energy of the system will also be conserved. Why does the second case never occur?



The second law of thermodynamics provides an answer to these types of questions. As mentioned the second law gives rise to another property of working fluids called *entropy*. Unlike energy, entropy is generally NOT a conserved quantity. Rather, in all real processes, the entropy of an appropriately defined system always *increases*. To put it another way processes that satisfy the first law but not the second are not possible (the above ship, paddle wheel, glass on table.). Most importantly of all the second law puts a theoretical limit on even the most perfect thermal machines.

CHAPTER 7: HEAT ENGINES

Heat Engines

Heat engines differ considerably in detail from one another but they all share the following characteristics:

They receive heat from a high temperature reservoir. They convert part of this heat to work. They reject the remaining (waste) heat to a low temperature reservoir. They operate in a cycle.

There are two types of heat engine; direct and reversed.



In a direct heat engine, Q_1 is supplied to the engine at temperature T_1 . Inside the engine, part of the heat transfer is converted to work (shown here as shaft work W_s). A quantity of heat Q_2 is rejected to a reservoir at temperature T_2 .

In a reversed heat engine, a work transfer *into* the device occurs. This shaft work is then used to pump heat from a low temperature reservoir at temperature T_2 into the high temperature reservoir at T_1 .

Examples of heat engines

Steam turbine power plant (direct heat engine)



In this example, the heat engine comprises of all the components lying within the system boundary. Notice that the steam turbine itself is NOT a heat engine, because work AND mass are transferred across the system boundaries of the turbine. The important mass transfers in this system are the fuel, air and exhaust gases.

Refrigerator (reversed heat engine)



In this example, heat transfer takes place between the working fluid and the evaporator located in the *ice box*. Fluid enters the condenser as a vapour at high pressure and (relatively) high temperature, where it condenses to a liquid phase at lower temperature. The cooled liquid flows through a throttle valve, where the pressure and temperature drop considerably (remember, a throttle valve is an *isenthalpic* process). The cold, low pressure fluid then draws heat from the ice box, which subsequently cools. As it is heated, the working fluid evaporates. The warmed vapour is then pumped up to the condenser pressure, where the process starts again. The heat engine is again

defined as all of those components lying within the system boundaries.

The refrigerator is an example of a **reversed** heat engine. Do NOT confuse the words **'reversed'** and **'reversible'**!

The refrigerator is called a reversed heat engine because work is transferred **into** the engine, and this work is used to transfer heat from a cold environment (ice box) to a warm environment (the room in which the fridge stands). The objective of a fridge is to *draw* heat *from* a low temperature reservoir and, using an input work transfer, *reject* this heat into a higher temperature environment.

A similar device to the fridge is the *heat pump*. This too is an example of a reversed heat engine. The objective of a heat pump is to take heat from a low temperature reservoir and, using an input work transfer, *use* it to provide (say) domestic heating.

Considering the example shown in Figure 3b. This reversed heat engine can be run either as a refrigerator or a heat pump. As a refrigerator transfer heat Q_2 from the ice box is the desired 'output'. As a heat pump, then transfer heat Q_1 to the house for domestic heating purposes is the desired output here.

Reversible processes

Processes in nature generally occur in one direction with time. As an example, a hot cup of coffee left on a table will eventually cool via conduction and convection. This process is *irreversible*, by which we mean that no matter how long we wait, the cold coffee in the cup will not spontaneously gather all the heat energy lost to the surroundings and warm itself.

A *reversible* process is one that can be made to take place in either forward or reverse directions by changing the conditions in the surroundings by ONLY an infinitesimal amount. A reversible process is a one that can be reversed without leaving any net effect on the surroundings.

Consider the following example:



Both processes (a) and (b) are *quasi-static*. In system (a), the pressure in the expanding bag is just sufficient to overcome the resistance of the mass (assuming no friction), which rises infinitely slowly. In system (b), the pressure in the bag is just sufficient to overcome the friction in the block, which slides infinitely slowly.

System (a) is reversible; by lowering the pressure in the bag by a very small amount, the system can be made to work in reverse. The potential energy in the mass can be recovered.

System (b) is irreversible; in doing work against friction, the displacement work in the bag is converted directly to heat. We cannot convert the thermal energy produced by friction into a means of recompressing the bag.

So what is meant by 'no net external effect on the surroundings'?

Consider again both systems (a) and (b) in Figure 6. After the masses have moved some arbitrary finite distance in both systems, the pressures in both bags are allowed to reduce by an infinitesimal amount. Consequently, the bags start to contract. To be reversible, the systems must return to their original respective states without any further input from the surroundings. At the end of the contraction process, we find

• System (a) is back exactly where it started with no further input-it is reversible.

• To get system (b) back into its initial configuration, we have to move the block back to its starting position. In order to do this we (as part of the surroundings) have to do further work on the block. This means that the expansion/contraction of the system has had an effect on us (the surroundings) and also the block. Energy has had to be withdrawn from the surroundings in order to return the system to its initial configuration and the block is now hotter than it was initially. The energy in the universe has been conserved—but it has changed 'character'. System (b) is therefore irreversible.

No processes in nature are reversible, so why do we study reversible processes?

They provide a theoretical limit for physical processes. It will be shown that even perfect (i.e. reversible) heat engines have thermal efficiencies of less than unity. These limits then serve as guides in the analysis and design of engineering applications.

The example above demonstrated that frictional processes lead to irreversibility. It can also be shown that if heat transfer takes place between two reservoirs with temperatures differing by a finite quantity ΔT , then there will be a resultant irreversibility. Only in the limit of heat transfer between two reservoirs whose temperatures differ by dT will the process become reversible.



Reversible heat engines

A reversible heat engine is one that involves no irreversibility as a result of friction or heat transfer across a finite temperature gradient. In the case of a direct



heat engine;

- We assume that the heat supplied to the 'top' of the engine is at T_1 no finite temperature gradient
- The heat rejected from the 'bottom' of the engine is at T_2 -- no finite temperature gradient
- The engine is **externally reversible**, because the heat transfer from the reservoirs (i.e. *external* to the engine) takes place reversibly (without finite temperature gradient).

The reversible heat engine is also **internally reversible**. As the name implies, the components of such an engine are frictionless and do not introduce transient phenomena such as pressure waves or pressure drops across valves.

CHAPTER 7: HEAT ENGINES

Statements of the second law of thermodynamics

The Kelvin-Planck statement of the second law of thermodynamics

It is impossible for any device that *operates in a cycle* to receive heat from a single reservoir and produce a net amount of work.

Schematically the second law is depicted as



Important observation:

The second law does not rely on any vague assumptions regarding friction or other irreversibility. It is a fundamental physical feature of work producing machines. Some of the heat supplied to a machine is ALWAYS rejected (wasted) to a low temperature reservoir. Note also that, like the first law, the second law of thermodynamics is an observational law. It cannot be derived rigorously from theory alone. Overwhelmingly however, experimental evidence supports the second law.

In summary, the first law and second law together state that

- The net work done by a heat engine = the net heat supplied
 - The gross heat supplied > the net work done.

An alternative, equivalent from of the second law is embodied in the Clausius statement;

The Clausius statement of the second law of thermodynamics

It is impossible to construct a device that *operates in a cycle* and produces no effect other than the transfer of heat from a lower temperature body to a higher temperature body.

The equivalence of the two statements is given in chapter 5 of Çengel and Boles but also re-examined after entropy is introduced.

The second law and efficiency

According to the first law of thermodynamics, heat and work transfers are forms of energy transfer, and energy is conserved. A thermodynamic system obeying the first law would look something like



The engine could be reversible or irreversible. In the case of a reversible engine, the 'efficiency' of such a device would be 100%. The engine would violate the second law.

The second law provides a meaning for the notion of **thermodynamic efficiency**. Efficiency is defined here as:



 $efficiency' = \frac{\text{what you want}}{\text{what you give}}$

It is usual in the discussion of heat engines to drop our usual sign convention for heat and work, and deal instead only with magnitudes. The directions of heat and work transfer are easily found by inspection

thermal efficiency of a heat engine $= \eta_{th} = \frac{W_s}{Q_1}$

coefficient of performance of a refrigerator $=\beta = \frac{Q_2}{W_s}$

coefficient of performance of a heat pump $=\beta' = \frac{Q_1}{W_s}$

Note that, for heat engines, $\eta_{th} < 1$, and the nomenclature is correct. For reversed heat engines, the 'efficiency' is effectively related to the reciprocal of η_{th} and in consequence is usually greater than one. The term *coefficient of performance* is used because efficiencies of greater than one are usually a sign of an incorrect calculation!

CHAPTER 7: HEAT ENGINES

Heat Engine efficiency: $\eta_{th} = \frac{W_s}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$ and by the second law $Q_2 > 0$ therefore $\eta_{th} < 1$

Refrigerators and heat pumps:

$$\beta = \frac{Q_2}{W_s} = \frac{Q_2}{Q_1 - Q_2} = \frac{Q_1 - Q_1 + Q_2}{Q_1 - Q_2} = \frac{Q_1}{Q_1 - Q_2} - 1 = \beta' - 1$$

so $\beta' = \beta + 1$, i.e. the coefficient of performance of a heat pump β' , is always 1.0 greater than that of a refrigerator β . This is because $Q_1 = Q_2 + W_s$.

Corollaries of the second law

It is possible to deduce a number of corollaries from the second law via logical argument. The first two of these corollaries are the most important, and these are referred to as **Carnot principles**.

Corollaries 1 and 2 (The Carnot principles)

1) The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs

2) The efficiencies of all reversible heat engines operating between the same two reservoirs are the same

(Sample proof given in appendix I)

Altogether, there are five main corollaries of the second law and corollary 3, in conjunction with the Carnot principles can be used to define the thermodynamic concept of **absolute temperature**.

Absolute temperature

Corollary 3

A temperature scale may be defined which is independent of thermometric substance

(Sample proof given in appendix II)

A consequence of the definition of the thermodynamic temperature scale is the result $\left(\frac{Q_2}{Q_1}\right)_{rev} = \frac{T_2}{T_1}$

pertaining to a reversible heat engine.

Reversible heat engines

$$\eta_{th} = \frac{W_s}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_2}{T_1}.$$

Reversible refrigerators and heat pumps

$$\beta' = \frac{Q_1}{W_s} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$
$$\beta = \frac{Q_2}{W_s} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$
$$\beta' = \beta + 1$$

From the equation for efficiency of a reversible heat engine, it is apparent that the most efficient heat engines are those that operate with the largest possible difference in temperatures between hot and cold reservoirs. In that case, $\frac{T_2}{T_1} \ll 1$, and η_{th} attains a high value. The idea that engines grow more efficient as the temperature ratio across them increases leads us to the idea that energy can have an associated quality.

Example Question:



For the two engines shown, calculate:

- 1) The work done
- 2) The heat rejected
- 3) The thermal efficiency

Solution:

For the left hand engine,

$$\eta_{th} = 1 - \frac{500}{1500} = \frac{2}{3} = 1 - \frac{Q_2}{Q_1}$$
$$W_s = \eta_{th}Q_1 = \frac{2}{3} \times 100 = 66.7 \text{kJ}$$
$$Q_2 = Q_1 - W_s = 33.3 \text{kJ}$$

For the right hand engine

$$\eta_{th} = 1 - \frac{500}{1000} = \frac{1}{2} = 1 - \frac{Q_2}{Q_1}$$
$$W_s = \eta_{th}Q_1 = \frac{1}{2} \times 100 = 50.0 \text{kJ}$$
$$Q_2 = Q_1 - W_s = 50.0 \text{kJ}$$

In both of these examples, the engines are supplied with the same quantities of heat energy. In the first case, the engine is able to do more work than in the second case. This is because the heat was supplied at a higher temperature. The quality of the heat supplied to a reversible heat engine is a measure of its capacity to do work. Hence, in the examples just quoted, the energy supplied to the first engine had a higher quality than that supplied to the second engine. When heat is transmitted across a finite temperature gradient, its quality is **degraded**.

Work is a higher quality of energy transfer than is heat. This is because all of the work input into a system can be converted to heat. However, not all the heat supplied to a system can be converted to work (the Kelvin-Planck statement of the second law). The concept of energy quality is closely tied to the thermodynamic property of **entropy**.

Appendix I: Proof of the Carnot principles

A proof by contradiction is provided here making use of the second law. Consider two engines (an irreversible engine and a reversible engine) operating between the same reservoirs. Assume that the irreversible engine has a greater efficiency than the reversible engine.



W, Hot reservoir Q Q W_{I} - W_{R} WR ЯE E_{I} (Q_2) $(Q_2)_{R}$ Cold reservoir

The hot reservoir supplies Q_1 to the irreversible engine, and is *supplied* with Q_1 from the reversible refrigerator. The hot reservoir supplies no net heat, and is effectively redundant. We can replace the original arrangement with the one shown here.

Turning now to the cold reservoir, we observe that the

cold reservoir receives $(Q_2)_I$ from the irreversible heat engine, and supplies $(Q_2)_R$ to the reversible refrigerator.



Both engines are supplied with equal quantities Q_1 of heat. By assumption $(\eta_{th})_{I} > (\eta_{th})_{P}$

and so

$$W_I > W_R$$

$$(Q_2)_I < (Q_2)_R$$

Now, suppose the reversible heat engine is ran as a refrigerator. The work consumed by the reversible refrigerator will be supplied by part of the output of the irreversible heat engine. A net quantity of work $W_I - W_R$ will be available from the heat engine/refrigerator arrangement.



Now, as $(Q_2)_I < (Q_2)_R$ by assumption, it follows that we can again replace the heat engine/refrigerator configuration with the one shown on the left. We can combine the heat engine/refrigerator pair to form a new, single heat engine. This is shown in the sketch as the dotted box.

What is evident is that our configuration is behaving as a single heat engine, producing a net quantity of work $(W_I - W_R),$ while being supplied with heat $(Q_2)_I - (Q_2)_R$ from a single (cold) reservoir. Such a device would violate the second law of thermodynamics

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(see the Kelvin-Planck statement). Consequently, our initial assumption must be wrong, i.e. it is not possible that $(\eta_{th})_I > (\eta_{th})_R$. Hence, corollary 1 follows.

One can obtain the proof of corollary 2 by exactly the same line of reasoning. In this case, however, we replace the irreversible heat engine with a second reversible heat engine. We then assume that this second engine has a greater efficiency, and proceed with the proof as before.

Appendix II: Absolute Temperature Scale

One of the consequences of the second Carnot principle is that the efficiency of a reversible heat engine is dependent **only** on the temperatures at which heat is supplied and rejected.



For a reversible heat engine, then $\eta_{th} = f(T_1, T_2)$ but, since $\eta_{th} = 1 - \frac{Q_2}{Q_1}$, it follows that $\frac{Q_2}{Q_1} = f(T_2, T_1)$. Suppose now we have three reversible heat engines

Suppose now we have three reversible heat engines configured as in Figure 11, and operating between the same hot and cold reservoirs.

Suppose that the two reversible heat engines 'A' and 'B'

are combined to make a single heat engine denoted by the dotted line. This 'combined' heat engine is reversible, as it is made of reversible components. In effect, we have two reversible heat engines working between the same two thermal reservoirs. Consequently, the heat supplied to the combined heat engine is the same as that supplied to heat engine 'C'.

For engine C the efficiency $\eta_{C} = f(T_1, T_3)$ and similarly for the two engines A and B, $\eta_{A} = f(T_1, T_2)$ and $\eta_{b} = f(T_2, T_3)$, where T_2 is the temperature at which heat is rejected from engine A. From these equations, it follows that

$$\frac{\underline{Q}_1}{\underline{Q}_2} = f(T_1, T_2)$$
$$\frac{\underline{Q}_2}{\underline{Q}_3} = f(T_2, T_3)$$
$$\frac{\underline{Q}_1}{\underline{Q}_3} = f(T_1, T_3)$$

Thus

$$f(T_1, T_3) = \frac{Q_1}{Q_3} = \frac{Q_1}{Q_2}\frac{Q_2}{Q_3} = f(T_1, T_2) \times f(T_2, T_3),$$

Now comes the clever bit! The left hand side of this equation is a function only of T_1 and T_3 . Therefore, the right hand side of the equation can only be a function of T_1 and T_3 . This can only be true if

$$f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)}$$
$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)},$$
$$f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

where ϕ is an arbitrary function. The selection of the function ϕ is entirely arbitrary, other than it must satisfy the previous relationships. Basically, any monotonic function is satisfactory, however. Kelvin suggested that $\phi(T) = T$ be used as a temperature scale in order to provide the relation

$$\left(\frac{Q_1}{Q_2}\right)_{rev} = \frac{T_1}{T_2}$$

It is worth remembering that this definition still does not give us a scale to work with, as it only defines the ratios of temperatures in reversible heat engines. In 1954, the Kelvin was defined via the triple point of water. At the international conference on weights and measures, the triple point of water was assigned the temperature of 273.16K. The magnitude of 1K was then defined as 1/273.15 of the temperature interval between absolute zero and the triple point temperature of water. To convert a temperature *t* measured in

 $^{\circ}$ C to a temperature *T* measured in K, we use

$$T = t + 273.15$$

Using the definition of absolute temperature provided by Kelvin, we have, for the following relations for efficiencies

Tutorial Questions

 Exhaust steam from a process plant is to be used as a source of heat for a heat engine. Steam is available at a pressure of 1.2 bars, dryness fraction 0.7. Heat transfer from the steam to the engine causes the steam to condense to a saturated liquid at 1.2 bars. River water is available at a mean temperature of 10°C. What is the maximum possible power that could be developed by the engine when exhaust steam mass flow rate is 4000 kg/hour.

[438.1kW]

[3525kJ]

- A refrigerator having a coefficient of performance two-thirds of that of a refrigerator operating on the reversed Carnot cycle works between a cold store at 10°C and a river at 20°C, which is used to cool the working fluid. If it requires 3 kW input to drive it, how much heat will it absorb from the cold store in one hour? [63.12MJ/Hr]
- 3. A reversible heat engine operates between two reservoirs at temperatures of 800 K and 300 K. The engine drives a reversible refrigerator which operates between reservoirs at temperature of 300 K and 250 K. The heat transfer to the heat engine is 1000 kJ. The net output of the combined engine-refrigerator plant is 100 kJ.
 - (i) What is the heat transfer from the reservoir at 250 K to the refrigerant? [2625kJ]
 - (ii) What is the net heat transfer to the reservoir at 300K?

CHAPTER 8

THE SECOND LAW: ENTROPY

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Read: Thermodynamics (An Engineering Approach by Cengel & Boles – 8th Ed.) - Chapter 7 "Entropy" pages 329-373.

Introduction

Recall that a microscopic description for entropy is possible, encapsulated quantitatively by the formula

 $S = k \ln W$,

where k is Boltzmann's constant and equals 1.38065×10^{-23} J/K and W is a measure of the number of ways the molecules of a system can be arranged to achieve the same total energy (the *weight* of an arrangement).

It is of interest to explore (in passing) the application of this formula for a simple system initially in contact with two thermal reservoirs as depicted in (1) with $T_2 > T_1$.

A linear temperature gradient is present in the system.



The entropy of the system in (1) is lower that that in (2) as a consequence of the inequality $W_1 < W_2$. This follows because in (1) high energy molecules must occupy positions on the right hand side with lower energy molecules placed on the left. In (2) however molecules are interchangeable and can be placed anywhere without affecting the total energy of the system. Both systems are assumed to have the same energy but $S_1 < S_2$ and in fact the system has moved in the direction of increasing entropy attaining a maximum at thermal equilibrium.

A form of the second law is that the entropy change of an isolated system always increases or, in the limit, stays the same.

The Origins of entropy

In the following, we will explore the consequences of corollaries 4 and 5, arising from the second law of thermodynamics. Corollary (4) gives the Clausius inequality, while corollary (5) provides the definition for the thermodynamic property of entropy.

Corollary 4 of the second law is

Corollary 4

Whenever a system executes a cycle, $\int_C \frac{\delta Q}{T} \le 0$

Proof:



A simplified proof is presented here to show the Clausius inequality. Consider the reversible engine shown in the sketch. Assume that the hot reservoir is at temperature T_1 , and the cold reservoir is at temperature T_2 . The first law applied to this engine provides

$$\int_C \delta Q = Q_1 - Q_2 = W_s > 0$$

Since T_1 and T_2 are constant, one can write

$$\int_C \frac{\delta Q}{T} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2},$$

But for a reversible heat engine $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ and hence, in summary

$$\oint \delta Q > 0$$
$$\oint \frac{\delta Q}{T} = 0$$

Replacing the reversible heat engine with an irreversible one supplied with the same quantity of heat. This is less efficient so

$$W_I < W_R$$

where the suffices I and R refer to irreversible and reversible, respectively. The inequality between irreversible and reversible work transfer implies

$$Q_{1} - (Q_{2})_{I} < Q_{1} - (Q_{2})_{R}$$
$$(Q_{2})_{I} > (Q_{2})_{R}$$

i.e. the heat rejected from an irreversible engine is greater than that rejected from a reversible engine. It follows that

CHAPTER 8: ENTROPY

$$\int_{C} \frac{\delta Q_{I}}{T} = \frac{Q_{1}}{T_{1}} - \frac{(Q_{2})_{I}}{T_{2}}, \qquad \frac{(Q_{2})_{I}}{T_{2}} > \frac{(Q_{2})_{R}}{T_{2}}$$
$$\frac{Q_{1}}{T_{1}} - \frac{(Q_{2})_{I}}{T_{2}} < \frac{Q_{1}}{T_{1}} - \frac{(Q_{2})_{R}}{T_{2}}, \qquad \int_{C} \frac{\delta Q_{I}}{T} < \frac{Q_{1}}{T_{1}} - \frac{(Q_{2})_{R}}{T_{2}}$$
$$\int_{C} \frac{\delta Q_{I}}{T} < \int_{C} \frac{\delta Q_{R}}{T} = 0 \Longrightarrow \int_{C} \frac{\delta Q_{I}}{T} < 0$$

In summary: for reversible engines; $\int_{C} \delta Q > 0$ but for irreversible engines; $\int_{C} \delta Q > 0$ $\int_{C} \frac{\delta Q}{T} = 0$

A slightly quicker approach to the analysis above is to note that:

$$\eta_I = 1 - \left(\frac{Q_2}{Q_1}\right)_I \le \eta_R = 1 - \frac{T_2}{T_1} \Longrightarrow \frac{(Q_1)_I}{T_1} - \frac{(Q_2)_I}{T_2} = \int_C \frac{\delta Q_I}{T} \le 0.$$

The crude "proof" above is only intended as an illustration and it is important to appreciate that the temperature in the Clausius inequality applies to the working fluid and not the reservoirs. No distinction was made in the "proof" although for a reversible engine these do in fact match.

Corollary 5

 $\int_{C} \frac{\delta Q_{R}}{T} = 0 \text{ for any reversible cyclic process. Hence } \int \frac{\delta Q_{R}}{T} \text{ is a$ **property** $of any reversible process}$ between a reference state 0 and any other state 1. This property is called **entropy**.



Proof

The first part of this corollary is a *verification* of the derivation performed for the previous corollary.

On the left is the diagram for two arbitrary cyclic processes. We have used the *p*-*v* merely for clarity—any two thermodynamic properties would do just as well as coordinates. The path the system follows initially is *1-A-2-B-1*. Suppose that the system is reversible. This implies that the heat and work transfers are equal in magnitude, but opposite in sign. The suffix 'R' is used to denote the fact that reversible heat and work transfers are being performed. When the process takes place in the forward direction 1-*A-2-B-1*, we have established that

$$\int_C \frac{\delta Q_R}{T} \le 0$$

Suppose we now run the system backwards. This is acceptable, as all the processes have taken place reversibly. The heat transfers change sign but remain the same magnitude. The cyclic integral in the reversed case becomes

$$\int_C \frac{\delta Q_R}{T} \ge 0$$

However, this relationship can ONLY satisfy corollary 5 if

$$\int_C \frac{\delta Q_R}{T} = 0$$

Hence this establishes the first part of the desired result.

The existence of entropy can be established in the same way as the existence of energy was established from the first law. Imagine *two* cycles drawn on a property diagram (as depicted in figure). We will denote those cycles here as *1-A-2-B-1*, and *1-A-2-C-1*. The letters denote the routes followed, and the numbers denote the end states. We assume that the cycles are reversible, and hence $\oint \frac{\delta Q_R}{T} = 0$ for each cycle. Expanding this integral out for the two cycles

$$\int_{1-A-2} \frac{\delta Q_R}{T} + \int_{2-B-1} \frac{\delta Q_R}{T} = 0$$
$$\int_{1-A-2} \frac{\delta Q_R}{T} + \int_{2-C-1} \frac{\delta Q_R}{T} = 0$$

Equating the two sides of this equation and simplifying, we find

$$\int_{2-B-1} \frac{\delta Q_R}{T} = \int_{2-C-1} \frac{\delta Q_R}{T}$$

Now, the end points are the same in both of these processes, but the routes followed differs—one route follows path 'B', while the other follows path 'C'. This means that the quantity $\frac{\delta Q_R}{T}$ must be a property. The property was named **entropy** by Rudolph Clausius in 1865, and was named after the Greek word $\tau\rho\sigma\pi\eta$, which means *transformation*. The entropy of a system is denoted by a letter s or S, and is defined

according to
$$dS = \frac{\delta Q_R}{T}$$
 or $ds = \frac{\delta q_r}{T}$ or $S = m \times s$ or $S_2 - S_1 = \int_1^2 \frac{\delta Q_R}{T}$.

It is **entropy**, and not energy alone, which is the important 'flowing quantity' in machines producing work.

The production of motive power is not due to the 'consumption' of entropy, but due to its *transportation* from hot bodies to cold ones

<u>Entropy determination using</u> $dS = \frac{\delta Q_R}{T}$ (or $ds = \frac{\delta q_R}{T}$)

Using the expression $dS = \delta Q_R/T$ is rather abstract as it involves imagining an artificial process for the reversible supply of heat.

Example1: Isobaric heating of H₂0

Consider the slow heating of a container of H₂O held at constant pressure as illustrated in the figure



Figure. Slow Isobaric Heating of fluid in a Cylinder

below.

Consider first the 1st law in incremental form, i.e. $du = \delta q - \delta \omega = \delta q - p dv$, which implies $\delta q = du + p dv = d(u + pv) = dh$. To apply $ds = \frac{\delta q_R}{T}$, we must relate this to $\delta q = dh$, which can be achieved for an imagined

reversible supply of heat from a reservoir of infinitesimal higher temperature than the system as illustrated in the figure.

Process 1-2: $\delta q_R = Tds = dh = c_p dT$ or $ds = c_p \frac{dT}{T}$, which integrates to give $s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) = 4.2 \ln\left(\frac{393}{273}\right) = 1.53$

kJ/kgK

In steam tables $s_f(@2bar) = 1.53 \text{ kJ/kgK}$.

Process 2-3: $\delta q_R = Tds = T_2ds = dh$ or $ds = \frac{dh}{T_2}$, which integrates

to give $s_3 - s_2 = s_{fg} = \frac{h_3 - h_2}{T_2} = \frac{h_{fg}}{T_2} = \frac{2202}{393} = 5.6 \text{ kJ/kg}$, as provided in the steam tables.



Example2: Hot Copper Block in a Lake

Consider further the placing of a copper block of mass m = 1 kg and of specific heat capacity c = 0.4 kJ/kgK in the centre of a very large lake. The temperature of the lake is $T^{\ell} = 300 \text{ K}$, whilst the initial temperature of the block is $T_1 = 350 \text{ K}$. The block cools and eventually matches the temperature of the lake, i.e. $T_2 = T^{\ell} = 300 \text{ K}$.

We would like to work out the entropy change of the universe consisting of the block and the lake for this process.

Consider first the 1st law in incremental form, i.e. $\delta Q = dU = mcdT$.

To apply
$$dS = \frac{\delta Q_R}{T}$$
, we must relate this to $\delta Q = mcdT$,

which can be achieved for an imagined reversible supply of heat from a reservoir with a temperature infinitesimally higher than the block.

This gives
$$mCdT = \delta Q_R = TdS$$
 or $dS = mc \frac{dT}{T}$, which

integrates to give:

$$\Delta S = mc \ln\left(\frac{T_2}{T_1}\right) = 1 \times 0.4 \ln\left(\frac{300}{350}\right) = -0.062 \text{ kJ/K} \text{ (Observe that entropy change can be negative!)}$$

Note also that the 1st law for the block integrates to give $Q_{1-2} = mc(T_2 - T_1) = 1 \times 0.4 \times (-50) = -20$ kJ. The negative sign is expected since energy in the form of heat leaves the block.

Let us now consider the entropy change for the lake and let us assume that the relationship $dS^{\ell} = \frac{\delta Q_R^{\ell}}{T^{\ell}}$ can be applied.

The temperature of the lake is constant, so the expression integrates to give $\Delta S^{\ell} = \frac{-Q_{1-2}}{T^{\ell}} = \frac{20}{300} =$

0.067 kJ/K.

Thus the entropy change for the universe is: $\Delta S^{univer} = \Delta S + \Delta S^{\ell} = -0.062 + 0.067 = 0.005 \text{ kJ/K}$

The Unsteady Flow Entropy Equation

Recall that the classical definition for entropy in differential form is $dS = \frac{\delta Q_R}{T}$, where δQ_R is an increment of heat reversibly applied. An increment in entropy can also be considered to be formed in two parts, i.e. $dS = \delta_e S + \delta_i S$, where $\delta_e S = \frac{\delta Q}{T}$ (called the exchange entropy) and $\delta_i S \ge 0$ is associated with entropy production and irreversibility. In the event of a reversible increment then $\delta_i S = 0$ and $dS = \delta_e S = \frac{\delta Q}{T} = \frac{\delta Q_R}{T}$. The relationship $dS = \delta_e S + \delta_i S$ is directly related to the Clausius inequality $\int_C \frac{\delta Q}{T} \le 0$, since

$$\int_{C} dS = 0 = \int_{C} \delta_{e} S + \int_{C} \delta_{i} S = \int_{C} \frac{\delta Q}{T} + \int_{C} \delta_{i} S \Longrightarrow \int_{C} \frac{\delta Q}{T} = -\int_{C} \delta_{i} S \le 0$$

where the result $\int_C dS = 0$ is a consequence of entropy being a property and a cyclic process.

A rate equation can also be written, i.e. $\dot{S} = \dot{S}_{e} \pm \dot{S}_{i}$, which is a form appropriate for a control volume although any transfer of entropy resulting from material transfer at the control surface must be accounted for.

Consider a control volume where an elemental volume of material exiting at dA is $\mathbf{v} \cdot \mathbf{n} dA dt$ from which it can be deduced that the elemental mass exiting is $\rho \mathbf{v} \cdot \mathbf{n} dA dt$ and it immediately follows that the elemental entropy exiting is $\rho \mathbf{v} \cdot \mathbf{n} dA dt$, which can be written as sdmdt.



The rate form of the entropy equation for an open system follows and is

$$\frac{dS_{cv}}{dt} + \int_{\Gamma} s dt \frac{\dot{q}}{J_{\Gamma}} \frac{\dot{q}}{T} + \dot{S}_{i}$$

where $S_{cv} = \int_{\Omega} sdm$ and $\dot{S}_i = \int_{\Omega} \dot{s}_i dm$, and for the case of a stationary control volume $d\dot{m} = \rho m n dA$. It is worth contrasting this with the transport equation for energy which is of the form

$$\frac{dE_{cv}}{dt} + \int_{\Gamma} edr = \int_{\Gamma} \frac{dt}{dt} + \int_{\Gamma} \frac{dt}{dt} +$$

where the right hand terms (heat and work rates) of this equation are interpreted as forms of energy transfer at the control surface.

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A similar interpretation is placed on $\int_{\Gamma} \frac{q}{T} dA$ in the entropy equation with is interpreted to be a form of entropy transfer. Note the absence of a work term in the entropy equation arising because work is an ordered form of energy transfer hence does not transfer entropy unlike heat which is a disordered form of energy transfer. The entropy transport equation includes a production term \hat{S}_i that captures entropy production in the control volume (arising from irreversibility). No such similar term is present in the energy equation as a consequence of the conservation of energy (the 1st law).

This approach is a rather modern interpretation on entropy (see Prigogine for a more detailed exposé).

Applications and Entropy production

It is of interest to apply the steady rate form of the entropy equation for an open system

$$\int_{\Gamma} s d\dot{m} = \int_{\Gamma} \frac{\dot{a}}{T} + \dot{S}_{i}$$

 $\int_{\Gamma} ed\dot{m} = \dot{Q} - \dot{W}_s$

along with the SFEE

to some of the devices previously considered.

Throttling

Entropy is defined via the expression $ds = \frac{\delta q_R}{T}$ but the heat flux is for a given reversible process in order to evaluate the change in entropy. All real world processes are irreversible!

How can we calculate the change in entropy for an irreversible process?



Consider a throttling process;

Applying the SFEE to the throttle gives

$$\int_{\Gamma} e^{h} d\dot{m} = \dot{m} \left(e^{h} = e^{h} \right) = 0 - 0 \Longrightarrow h_{2} = h_{1}$$

Similarly for entropy

$$\int s d\dot{m} = \dot{m} \left[s_{2} - s_{1} \right] = 0 + \dot{s}_{i} = s_{1} = \frac{S_{i}}{\dot{m}} = s_{i} > 0.$$

where s_i is an entropy production term. It has NO analogy with any other field of science. The term represents a degradation in the quality of the energy-the capacity of the energy to do work has diminishes as a result of flowing through the throttle.





Applying the SFEE to the nozzle gives

$$\int_{\Gamma} e^{h} d\dot{m} = \dot{m} \left(e^{h}_{2} = e^{h}_{1} \right) = 0 - 0 \Longrightarrow h_{2} + \frac{1}{2} v_{2}^{2} = h_{1} + \frac{1}{2} v_{1}^{2} \text{ and similarly for entropy}$$
$$\int_{\Gamma} s d\dot{m} = \dot{m} \left(s_{2} - s_{1} \right) = 0 + 0 \Longrightarrow s_{2} = s_{1}.$$

The process can, to a reasonable approximation, be assumed to be isentropic (constant entropy). Note that reversible and adiabatic implies isentropic.

This follows because reversible gives $dS = \delta_e S = \frac{\delta Q_R}{T}$ and adiabatic gives $\delta Q_R = 0$, so dS = 0. However, isentropic does not necessarily imply reversible or adiabatic since dS = 0 gives $\delta_e S + \delta_i S = 0$ or $\delta_e S = -\delta_i S \neq 0$, if the process happens to be irreversible.

Turbine



Applying the SFEE to the turbine gives

$$\int_{\Gamma} e^{h} d\dot{m} = \dot{m} \left(e^{h}_{\frac{1}{2} = e^{h}} \right) = 0 - \dot{W}_{s} \Longrightarrow h_{2} - h_{1} = -\frac{\dot{W}_{s}}{\dot{m}} = -w_{s} \text{ and similarly for entropy}$$

$$\int s d\dot{m} = \dot{m} \left(s_{\frac{1}{2} - s_{1}} \right) = 0 + 0 \Longrightarrow s_{2} = s_{1}.$$

The process can again to a reasonable approximation be assumed to be isentropic (constant entropy).

Heat Exchangers



Applying the SFEE to the heat exchanger gives

$$\int e^{h} d\dot{m} = 0 \implies \dot{m}^{f} \left(\dot{h}_{out}^{c} - \dot{h}_{in}^{c} \right) + \dot{m}^{c} \left(\dot{h}_{out}^{c} - \dot{h}_{m}^{c} \right) = 0 \text{ and similarly for entropy}$$
$$\int s d\dot{m} = \dot{B}_{i} \implies \dot{S}_{i} = d \left(\frac{c}{bu} - \frac{c}{m} \right) = d \left(\frac{c}{bu} - \frac{c}{m} \right) = 0$$

Entropy production takes place inside the heat exchanger signalling that the heat-exchange process is irreversible. The presence of finite temperature differences signals irreversibility (lost work) since the heat transfer taking place could in principle have been used to produce work (i.e. by using a reversible heat engine).

Example question: (on energy degradation)

Steam at 60bar, dry saturated is fed into a turbine via a throttle valve. The steam leaves the turbine at 0.08 bar and the turbine is ISENTROPIC (the entropy does not change as it flows through the turbine).

Derive an equation for the turbine work

Calculate the steam mass flow rate if the turbine is to produce 10MW

- a) Without the throttle valve.
- b) If the steam is throttled to 40 bar prior to entering the turbine.

Calculate the enthalpies and entropies before and after the valve, and after the turbine.

Solution:

(a) Recall the SFEE $\int e^{h} d\dot{m} = \dot{Q} - \dot{W}_{s}$ which for a turbine reduces to $\dot{m} [h_{2} - h_{1}] = -\dot{W}_{s}$ or

$$\dot{W}_{s} = -i \dot{H} h_{2} - h_{1}$$

At 60 bar (page 7 or page 5): $T_s = 275.6 \,^{\circ}C$, $h_1 = h_g = 2784 \, kJ/kg$ and $s_1 = s_g = 5.890 \, kJ/kgK$. Since the turbine is isentropic $s_2 = s_1 = 5.890 \, kJ/kgK$. Examination of page 3 at $p_2 = 0.08$ bar reveals $s_g = 8.227 \, kJ/kgK$ and $s_f = 0.593 \, kJ/kgK$. Similar triangles gives $\frac{h_2 - h_f}{h_{fg}} = \frac{s_2 - s_f}{s_{fg}} = \frac{5.890 - 0.593}{7.634} = 0.694$. Thus, $h_2 = h_f + 0.694 \times h_{fg} = 174 + 0.694 \times 2402 = 1841 \, kJ/kg$. It immediately follows that $\dot{m} = -\frac{\dot{W}_s}{h_2 - h_1} = -\frac{10000}{1841 - 2784} = 10.6 \, kg/s$.

(b) Recall that the throttling process is an isenthalpic process on neglect of kinetic energy components. Thus at 40 bar the enthalpy at the entrance of the turbine (and exit of throttle) is $h_1 = 2784 \text{ kJ/kg}$. Examination of page 4 (at 40 bar) reveals $h_g = 2801 \text{ kJ/kg}$ along with $T_s = 250.3 \,^{\circ}\text{C}$. Similar triangles gives $\frac{s_1 - s_f}{s_{fg}} = \frac{h_1 - h_f}{h_{fg}} = \frac{2784 - 1087}{1714} = 0.99$. Thus, $s_1 = s_f + 0.99 \times s_{fg} = 2.797 + 0.99 \times 3.273 = 6.04 \text{ kJ/kgK}$. Since the turbine is isentropic $s_2 = s_1 = 6.04 \text{ kJ/kgK}$. Repeating the process above for $p_2 = 0.08$ bar reveals $\frac{h_2 - h_f}{h_{fg}} = \frac{s_2 - s_f}{s_{fg}} = \frac{6.04 - 0.593}{7.634} = 0.714$. Thus, $h_2 = h_f + 0.694 \times h_{fg} = 174 + 0.714 \times 2402 = 1889 \text{ kJ/kg}$. It immediately follows that $\dot{m} = -\frac{\dot{W}_s}{h_2 - h_1} = -\frac{10000}{1889 - 2784} = 11.2 \text{ kg/s}$. Energy degradation manifests as an increase in

mass flow rate to obtain the same power output from the turbine.

Example Question (entropy change in vapours):

Ammonia, initially at 2°C and with a dryness fraction of 0.1 is heated until it reaches the dry saturated state. Evaluate the change of entropy.

Solution: Turn to page 13 and observe at $T = 2^{\circ}C$, $s_f = 0.749 \text{ kJ}/\text{kgK}$ and $s_g = 5.314 \text{ kJ}/\text{kgK}$, and it follows that $s = s_f + x (s_g - s_f) = 0.749 + 0.1(5.314 - 0.749) = 1.2 \text{ kJ/kgK}$ and $s_g - s = (s_g - s_f) - x(s_g - s_f) = (s_g - s_f)(1 - x) = (5.314 - 0.749) \times 0.9 = 4.11 \text{ kJ/kgK}$ (or simply sg - s = 5.314 - 1.2 = 4.11 kJ/kgK)

Example Question (entropy change in vapours):

Dry saturated steam at a pressure of 10 bar is supplied to a turbine. If the turbine expands the steam to a pressure of 1 bar, calculate the quality of the steam leaving the turbine, and the shaft power produced for a flow rate of 15kg/s

Solution: Recall the SFEE $\int e^h d\dot{m} = \dot{Q} - \dot{W}_s$ which for a turbine reduces to $\dot{m} [h_2 - h_1] = -\dot{W}_s$ or

$$\dot{W}_s = -i \dot{m} h_2 - h_1$$
).

At 10 bar (page 7 or page 4): $T_s = 179.9 \ ^{0}C$, $h_1 = h_g = 2778 \ kJ/kg$ and $s_1 = s_g = 6.586 \ kJ/kgK$. Since the turbine is isentropic $s_2 = s_1 = 6.586 \ kJ/kgK$.

Examination of page 4 at $p_2 = 1.0$ bar reveals $s_g = 7.359 \text{ kJ/kgK}$ and $s_f = 1.303 \text{ kJ/kgK}$. Similar triangles gives $\frac{h_2 - h_f}{h_{fg}} = \frac{s_2 - s_f}{s_{fg}} = \frac{6.586 - 1.303}{6.056} = 0.872 = x$. Thus, $h_2 = h_f + 0.872 \times h_{fg} = 417 + 0.872 \times 2258 = 2386 \text{ kJ/kg}$. It immediately follows that $\dot{W}_s = -15 \times (2386 - 2778) = 5880 \text{ kW}$.

Entropy as a property

Since entropy is a property it can be related to other properties via the two-property rule, so can be read from steam tables or related via a *thermodynamic identity*.

The Central Equation of Thermodynamics

For a closed system, energy transfers that take place can be evaluated from the First Law (in terms of specific quantities), i.e.

$$du = \delta q - \delta w$$

For a reversible process involving a resisted expansion with reversible heat transfer $\delta w = pdv$ and $\delta q_R = Tds$, which on substitution leads to a rather important equation (sometimes referred to as the *central equation of thermodynamics*), i.e.

$$Tds = du + pdv$$
 (or $TdS = dU + pdV$)

Observe that this equation only involves state variables and consequently applies for all processes (on simple systems) irrespective of whether or not the process is reversible. This is a significant advance since this equation provides a general relationship between p, v, T and s. It is in essence a *thermodynamic identity* since it is not necessary to inquire whether the process is reversible or irreversible to apply it.

Note also that h = u + pv, giving dh = du + pdv + vdp which on substitution gives

$$Tds = dh - vdp$$

Entropy for solids and liquids

Under the assumption that a solid or liquid is incompressible, then dv = 0 and the central equation of thermodynamics (Tds = du + pdv) reduces to Tds = du.

Setting du = cdT for a constant specific heat capacity c, we obtain $ds = c \frac{dT}{T}$, which integrates to give

$$s_2 - s_1 = c \ln \left(\frac{T_2}{T_1}\right)$$

which is a relatively simple relationship for determining specific entropy change for an incompressible solid or liquid.

Entropy for ideal gases

When dealing with vapours, entropy changes can be found using the steam tables. For ideal gases, analytic relations can be written down for the entropy change during a process in terms of other properties.

The starting equation is the all-important *central equation of thermodynamics*, i.e. Tds = du + pdv and in view of the identities pv = RT and $du = c_v dT$, this equation transforms into

$$ds = c_v \frac{dT}{T} + \frac{p}{T} d\nu = c_v \frac{dT}{T} + R \frac{d\nu}{\nu}.$$

If the gas is **perfect**, then (by definition) $c_v = const.$ and this relation can be integrated directly to obtain

$$s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)$$

From the definition of a specific quantity, S = ms and hence it follows that

$$S_2 - S_1 = m \left(c_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right) \right)$$

If the gas is **ideal**, then $c_v = c_v(T)$, and

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T} dT + R \ln\left(\frac{v_2}{v_1}\right).$$

An alternate but equivalent equation for the change of entropy can be derived from the equation $Tds = dh - \nu dp$, which on substitution of $p\nu = RT$ and $dh = c_p dT$ gives

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p}$$

For a **perfect** gas, integration of this relationship provides

$$s_{2} - s_{1} = c_{p} \ln\left(\frac{T_{2}}{T_{1}}\right) - R \ln\left(\frac{p_{2}}{p_{1}}\right)$$
$$S_{2} - S_{1} = m\left(c_{p} \ln\left(\frac{T_{2}}{T_{1}}\right) - R \ln\left(\frac{p_{2}}{p_{1}}\right)\right)$$

whilst for an **ideal** gas, $c_p = c_p(T)$ and

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT - R \ln\left(\frac{p_2}{p_1}\right)$$

The isentropic process in a perfect gas

Recall that an isentropic process is one in which ds = 0 and in the case of a perfect gas

$$ds = 0 = c_{v} \frac{dT}{T} + R \frac{dv}{v} = c_{p} \frac{dT}{T} - R \frac{dp}{p}$$
$$0 = c_{v} \left(\frac{dT}{T} + (\gamma - 1)\frac{dv}{v}\right) = c_{p} \left(\frac{dT}{T} - \frac{(\gamma - 1)}{\gamma}\frac{dp}{p}\right)$$

where γ the ratio of specific heats is $\gamma = \frac{c_p}{c_v}$ and where use is made of $R = c_p - c_v$.

Integrating these equations gives us two equivalent ways of specifying an isentropic process. One way specifies the process in terms of T and v, while the other specifies the process in terms of T and p.

$$0 = \ln\left(\frac{T_2}{T_1}\right) + (\gamma - 1)\ln\left(\frac{\nu_2}{\nu_1}\right) = \ln\left(\frac{T_2}{T_1}\right) - \frac{(\gamma - 1)}{\gamma}\ln\left(\frac{p_2}{p_1}\right)$$
$$= \ln\left(\frac{T_2\nu_2^{\gamma - 1}}{T_1\nu_1^{\gamma - 1}}\right) = \ln\left(\frac{T_1p_1^{\left(\frac{\gamma - 1}{\gamma}\right)}}{T_2p_2^{\left(\frac{\gamma - 1}{\gamma}\right)}}\right)$$

This then implies that an isentropic process is one that satisfies

$$Tv^{\gamma-1} = const.$$
 or $Tp^{\left(\frac{1-\gamma}{\gamma}\right)} = const.$

Finally, an isentropic process can also be described by using the ideal gas equation of state in either of the above two equations to obtain

$$pv^{\gamma} = const.$$

In most engineering applications, this last equation is the most common way of expressing an isentropic process

An isentropic process in a perfect gas satisfies:

$$Tv^{\gamma-1} = \text{const.}, \quad Tp^{\left(\frac{1-\gamma}{\gamma}\right)} = \text{const.}, \quad pv^{\gamma} = \text{const.}$$

Example Question:

Air, initially at 298K is reversibly heated to 505K. If the heating process is isochoric, calculate

- a) The change in entropy of the gas
- b) The heat supplied for kg of gas

For air, assume perfect gas behaviour, with R=287J/kgK, $c_v = 718$ J/kgK and $\gamma = 1.4$

Solution:

(a) The starting equation is the *central equation of thermodynamics*, i.e. Tds = du + pdv and in view of the identities pv = RT and $du = c_v dT$, this equation transforms into

$$ds = c_v \frac{dT}{T} + \frac{p}{T} dv = c_v \frac{dT}{T} + R \frac{dv}{v} = c_v \frac{dT}{T}, \text{ which integrates to give}$$
$$s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) = 718 \times \ln\left(\frac{505}{298}\right) = 378.72 \text{ kJ/kgK}.$$

(b) In view of the fact that the process is reversible $\delta q_R = Tds$, where $ds = c_v \frac{dT}{T}$, which yields

$$\delta q_{R} = c_{v} dT$$
. This integrates to give
$$q_{1-2} = \int_{T_{1}}^{T_{2}} c_{v} dT = c_{v} (T_{2} - T_{1}) = 718 \times (505 - 298) = 148.6 \text{ kJ/kg}$$

Example question: Demonstrate for an ideal gas (i.e. one satisfying pv = RT) that the intrinsic specific internal energy u is a function of temperature only.

Solution: Experimental evidence for this was presented in previous notes but it is of interest to confirm whether this can be established analytically with knowledge of the state equation pv = RT and the central equation of thermodynamics Tds = du + pdv.

Assume initially that
$$u = u(T, v)$$
 along with $s = s(T, v)$. It follows that $du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$

and likewise $ds = \left(\frac{\partial s}{\partial T}\right)_{v} dT + \left(\frac{\partial s}{\partial v}\right)_{T} dv$. Substitution into Tds = du + pdv gives $T\left(\frac{\partial s}{\partial T}\right)_{v} dT + T\left(\frac{\partial s}{\partial v}\right)_{T} dv = \left(\frac{\partial u}{\partial T}\right)_{v} dT + \left[\left(\frac{\partial u}{\partial v}\right)_{T} + p\right] dv$

In view of the independence of T and v it follows that $T\left(\frac{\partial s}{\partial T}\right)_{v} = \left(\frac{\partial u}{\partial T}\right)_{v} = c_{v}$ and $T\left(\frac{\partial s}{\partial v}\right)_{T} = \left(\frac{\partial u}{\partial v}\right)_{T} + p$, which can also be written as $\left(\frac{\partial s}{\partial v}\right)_{T} = \frac{1}{T}\left(\frac{\partial u}{\partial v}\right)_{T} + \frac{p}{T} = \frac{1}{T}\left(\frac{\partial u}{\partial v}\right)_{T} + \frac{R}{v}$.

The next step is a little tricky but differentiation of this expression with respect to T gives

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 $\frac{\partial^2 s}{\partial T \partial \nu} = \frac{1}{T} \frac{\partial^2 u}{\partial T \partial \nu} - \frac{1}{T^2} \left(\frac{\partial u}{\partial \nu} \right)_T \text{ but this must match } \frac{\partial^2 s}{\partial \nu \partial T} = \frac{1}{T} \frac{\partial^2 s}{\partial \nu \partial T}, \text{ which is obtained on}$ differentiation of $\left(\frac{\partial s}{\partial T} \right)_{\nu} = \frac{1}{T} \left(\frac{\partial u}{\partial T} \right)_{\nu}$ with respect to ν . It immediately follows that $\left(\frac{\partial u}{\partial \nu} \right)_T = 0$ or to put it another way u = u(T).

<u>T-s diagrams</u>

Recall that two independent thermodynamic properties are sufficient to characterise the thermodynamic state of a simple system. Although restricting our attention thus far to p-v, T-v or p-T graphs it is possible utilise entropy too as an independent variable in describing thermodynamic processes. Of particular interest is the plotting of processes on T-s diagrams.

Observe that with a process on a p-v diagram then, providing certain restrictions are adhered to (i.e. quasistatic behaviour) then the area under the curve is equal to the work done by the process. By analogy, with a process on a T-s diagram, and provided certain restrictions are adhered to (i.e. the process is *reversible*), then the area under the curve can be equated to the heat transfer during the process.

Reversible processes on the T-s diagram



Recall that
$$ds = \frac{\delta q_R}{T}$$
, or equivalently $\delta q_R = Tds$.

Consider a system undergoing a reversible change of state and let us draw that change of state on a T-s diagram.

As the system passes through a sequence of equilibrium states, a quantity of heat is transferred to the system δq_R .

The total area under the curve is: $q_{1-2} = \int_{1}^{2} Tds$ for a *reversible* process.

Reversible, adiabatic (isentropic processes)



A particularly important process, which is encountered many times in thermodynamics, is an *isentropic* process. An isentropic process is one in which the entropy of the system does not change

Since $ds = \frac{\delta q_R}{T}$, where δq_R is the reversible heat flux. As our system is reversible *and* adiabatic,

$$\delta q = \delta q_{\rm p} = 0$$

hence ds = 0.

On the T-s diagram, *isentropes* appear as vertical lines.

Irreversible processes



For irreversible processes
$$(q \neq q_R)$$

 $ds > \frac{\delta q}{T}$
It follows immediately that
 $q_{1-2} \neq \int_{1}^{2} T ds$

for irreversible processes.

The way we remind ourselves of this fact is as follows. In the sketch on the left, the (unknown) irreversible path is drawn as a dotted line joining state points 1 and 2. The shaded area under the curve (which, for a reversible process represents the heat transfer) can 'escape' through the dotted lines and hence $\delta q \neq T ds$.

In summary:

- Entropy change between any two state points can always be evaluated, because entropy is a property
- Entropy change and absolute temperature cannot always be related to the actual heat supplied to the system. Heat transfer and entropy changes are only related for *reversible* processes.

T-s diagram for perfect gases

For a particular perfect gas the following processes are of particular interest:

- 1. Isothermal
- 2. Reversible adiabatic
- 3. Isobaric
- 4. Isochoric
- 1. Isothermal process

This implies that during the process, dT = 0. Hence an isothermal process on the T-s graph is horizontal



2. Reversible adiabatic process

A process which is reversible and adiabatic is isentropic, hence ds = 0. An isentropic process on the T-s diagram is vertical

3. Isobaric process

Starting from the relation

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p}$$

We observe that dp = 0. Integrating the equation (recall the gas is perfect and hence $c_v = \text{const.}$) gives

$$\mathbf{s}_2 - \mathbf{s}_1 = \mathbf{c}_p \ln\left(\frac{\mathbf{T}_2}{\mathbf{T}_1}\right)$$

rearranging this provides

$$T_2 = T_1 \exp\left(\frac{s_2 - s_1}{c_p}\right)$$

4. Isochoric process

Given

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

and for an isochoric process $\,d\nu=0$, and on integration yields

$$T_2 = T_1 \exp\left(\frac{s_2 - s_1}{c_v}\right)$$



Note that the only difference between the isochoric and isobaric processes is the specific heat used in the exponential. Since $c_p > c_v$ it follows that for a given initial temperature T_1 , and a given change in entropy $s_2 - s_1$, an isochoric process has a higher final temperature than an isobaric process, i.e. the curves of the isochors on a T-s diagram are always steeper than the curves of the isobars.

MODERN THERMODYNAMICS







Heat Engines revisited

Let us revisit heat engines to test out the new version of the 2nd law.

Consider the possibility of a heat engine operating in a cycle but supplied only from a single thermal reservoir at temperature T_1 – this is ruled out by the Kelvin-Planck version of the 2nd law.



The entropy change in the thermal reservoir $\Delta S_1 = -\frac{Q_1}{T_1}$ is the only entropy change that is taking place. The entropy flows out of the reservoir in the form $-\frac{Q_1}{T_1}$ into a device that suffers no net entropy change (operating on a cycle). The entropy of the universe considered here suffers a net decrease in

entropy, i.e. $\Delta S = \Delta S_1 = -\frac{Q_1}{T_c} < 0$, but this is contrary to the 2nd law, thus not possible.



Consider the Clausius version of the 2nd law (as depicted in the diagram) rules out the possibility of a cyclic device being able to transfer heat from a cold body to a hot body without work.

In this case the total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = Q_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) < 0, \text{ since}$$

 $T_2 < T_1$, which is contrary to the 2nd law.

In the case of a reversible engine as that depicted in the figure below, the total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \text{, since } \frac{T_2}{T_1} = \frac{Q_2}{Q_1}$$



More generally
$$\Delta S = \Delta S_1 + \Delta S_2 = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \ge 0$$
, which
implies $-\frac{Q_2}{Q_1} \le -\frac{T_2}{T_1}$ and $1 - \frac{Q_2}{Q_1} \le 1 - \frac{T_2}{T_1}$ hence $\eta_{th} \le \eta_R$.

This proves that Carnot engines are the most efficient and the reason why is that entropy is not produced.

Heat *spontaneously* flows from a hot to a cold body and such spontaneity can be used to produce work.

T-s diagrams and cyclic processes

The plant layout for a vapour cycle power plant is depicted below along with how we would represent this configuration as a heat engine operating between two thermal reservoirs (i.e. a 'direct' heat engine).



Assume that all components of the plant are internally and externally reversible. From the first law applied to the plant $\int_C \delta W = \int_C \delta Q$ and, furthermore $\int_C \delta Q = \int_C T dS$.

It follows that the work done during a reversible cyclic process is represented by the area enclosed on a *T*-s diagram.

T-s diagram for a pure substance

A *T* - *s* diagram for a substance which changes phase during heating is depicted in the figure below.



Two constant pressure lines are shown on the diagram. At the lower pressure, the fluid is first heated as a liquid until it reaches the saturated liquid line. At this point further heating does not raise the temperature, but provides the latent heat of evaporation. After reaching the saturated vapour line, the fluid temperature rises as heating continues. At the higher pressure (which, here, is above the critical pressure), the fluid does not go through an evaporation process, and passes from the 'liquid' to 'vapour' phase without addition of latent heat.


In the power plant configuration shown above, the *T*-s diagram appears as below

There are two types of reversible process shown in the figure above.

- i. Isothermal reversible processes: these are processes that take place at constant temperature, and are depicted by lines ab and cd on the T s diagram.
- **ii.** Adiabatic, reversible processes: these are processes that take place at *constant entropy* on the *T-s* diagram. As mentioned previously, these lines are called *isentropes*, and the processes are termed *isentropic*. Remember, all reversible, adiabatic processes are isentropic, but not all isentropic processes are reversible or adiabatic.

The four processes shown on the figure make up a process, a-b-c-d-a, and this is the process undertaken by the working fluid in the reversible heat engine formed by our power plant. The cycle consists of:

- two isothermal processes, a-b (in the boiler) and c-d (in the condenser);
- two isentropic processes, d-a (in the feed pump) and b-c (in the turbine).

These processes are all reversible, and hence $\delta q_R = T ds$ for unit mass.

For the isotherm, a-b:
$$[q_R]_{ab} = \int_a^b T ds = T_a (s_b - s_a).$$

For the isentrope, b-c: $[q_R]_{bc} = \int_a^c T ds = 0$, because $ds = 0$

For the isotherm, c-d: $[q_R]_{cd} = \int_{a}^{d} T ds = T_c (s_d - s_c).$

For the isentrope, d-a:
$$[q_R]_{da} = \int_{d}^{a} T ds = 0$$
, because $ds = 0$.

Hence, for the cycle:

$$\int_{C} \delta q_{R} = [q_{R}]_{ab} + [q_{R}]_{bc} + [q_{R}]_{cd} + [q_{R}]_{da}$$
$$= T_{a} (s_{b} - s_{a}) + 0 + T_{c} (s_{d} - s_{c}) + 0$$

but $(s_b - s_a) = -(s_d - s_c)$, and thus

 $\int_{C} \delta q_{R} = (T_{a} - T_{c})(s_{b} - s_{a}) = \text{area of cycle } a - b - c - d \text{ on the } T - s \text{ diagram}$

Now, from the First Law, $\int_C \delta q_R = \int_C \delta w$, and hence $\int_C \delta w = (T_a - T_c)(s_b - s_c)$.

Recapping with reference to the processes shown in the figure:

- For a reversible cycle, the work done is the area enclosed on the *T-s* diagram, i.e. it is depicted by the area a-b-c-d-a;
- The heat supplied to a reversible cycle is depicted by the area a-b-f-e-a;
- The heat rejected from a reversible cycle is depicted by the area d-c-f-e-d.



The efficiency of a reversible cycle is given by:

$$\eta = \frac{\text{Work done}}{\text{Heat supplied}} = \frac{\left(T_{a} - T_{c}\right)\left(s_{b} - s_{a}\right)}{T_{a}\left(s_{b} - s_{a}\right)} = \frac{T_{a} - T_{c}}{T_{a}} = 1 - \frac{T_{c}}{T_{a}}$$

This value of efficiency is in agreement with that obtained from the definition of absolute temperature.

The cycle undergone by the working fluid in our power plant is referred to as a **Carnot cycle**. Engine cycles are discussed in greater detail in the 2^{nd} year. The Carnot cycle is an *ideal* engine cycle, and cannot be realised in practice.

Example Question:

An aircraft gas turbine comprises the following pieces of equipment: i) a compressor, ii) a combustion chamber, iii) a turbine, and iv) a propelling nozzle.

(a) Draw a schematic of the gas turbine.

(b) Air is drawn into the turbine at a pressure of 1bar, 278K. At the outlet of the compressor, the pressure is 10 times greater than at inlet. In the combustion chamber, the gas is heated at constant pressure to 1500K whereupon it is fed into the turbine. If the work produced by the turbine must be the same as that consumed by the compressor, find the temperature and pressure ratios across the turbine.

(c) Plot the process undergone by the air as it passes through the engine from inlet to turbine exhaust on a *T-s* diagram.

For air, assume perfect gas behaviour, with R = 287 J/kgK, $c_v = 718$ J/kgK and $\gamma = 1.4$

Solution:

(a) A schematic for the gas turbine (excluding the nozzle) is:



(b) Let us consider each component in turn and assume steady condition so the SFEE applies, i.e. $\int e^h d\dot{m} = \dot{Q} - \dot{W}_s \text{ or } \Delta e^h = q - w_s$

The **compressor** can be assumed to be isentropic and satisfies $h_2^c - h_1^c = -w_s^c$ and in view of the identity $dh = c_p dT$ it follows that $h_2^c - h_1^c = c_p (T_2^c - T_1^c) = -w_s^c$. Recall that for an isentropic process:

$$\frac{T_2^c}{T_1^c} = \left(\frac{p_2^c}{p_1^c}\right)^{\left(\frac{\gamma-1}{\gamma}\right)} = \left(\left(\frac{10}{1}\right)^{\left(\frac{1.4-1}{1.4}\right)}\right) = 10^{\frac{2}{7}} \Longrightarrow T_2^c = T_1^c \times 10^{\frac{2}{7}} = 278 \times 10^{\frac{2}{7}} = 536.7 \text{K}.$$

For the combustion chamber the SFEE reduces to

$$h_2^b - h_1^b = q^b$$
 or $c_p (T_2^b - T_1^b) = q^b$.

For the **turbine**

$$\mathbf{h}_{2}^{t} - \mathbf{h}_{1}^{t} = \mathbf{c}_{p} \left(\mathbf{T}_{2}^{t} - \mathbf{T}_{1}^{t} \right) = -\mathbf{w}_{s}^{t}$$

and in view of the requirement that $w_s^t = -w_c^t$ it follows that

$$T_2^t - T_1^t = -(T_2^c - T_1^c) \Longrightarrow T_2^t = T_1^t + T_1^c - T_2^c = 1500 + 278 - 536.7 = 1241.3K$$

Assuming an isentropic process for the turbine gives

$$\left(\frac{p_2^t}{p_1^t}\right) = \left(\frac{T_2^t}{T_1^t}\right)^{\left(\frac{\gamma}{\gamma-1}\right)} = \left(\left(\frac{1241.3}{1500}\right)^{\left(\frac{1.4}{1.4-1}\right)}\right) = 0.83^{\frac{7}{2}} \Longrightarrow p_2^t = p_1^t \times 0.83^{\frac{7}{2}} = 10 \times 0.83^{\frac{7}{2}} = 5.21 \text{bar}$$

(c) T-s diagram of the process:



CHAPTER 8: ENTROPY

READING EXERCISE: The entropy change of the universe

In the following subsection, we discuss the final corollary of the second law

Corollary 6

The entropy change of an isolated system always increases or, in the limit, stays the same

Proof:

Consider two bodies at different temperatures



Assume that $T_1 > T_2$, and that the heat transfer takes place reversibly. Now,

$$dS_1 = -\frac{\delta Q}{T_1} \text{ for body 1}$$
$$dS_2 = \frac{\delta Q}{T_2} \text{ for body 2}$$

The *quantity* of energy in the system is conserved—the first law is obeyed. Let us examine the total change of entropy for the two bodies

$$\begin{split} d\mathbf{S} &= d\mathbf{S}_1 + d\mathbf{S}_2 = \delta \mathbf{Q}_1 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ &= \delta \mathbf{Q}_1 \left(\frac{T_1 - T_2}{T_1 T_2} \right) \end{split}$$

Here, δQ represents the magnitude of the heat transfer. As $T_1 > T_2$, it follows that

$$dS = \delta Q_1 \left(\frac{T_1 - T_2}{T_1 T_2} \right) > 0$$

The entropy of the combined system has increased. When we are describing changes in entropy, reference is often made to the **entropy change of the universe**. This seems like a daunting concept, but is really quite straightforward. The analysis just conducted has been on two thermodynamic systems. There is no reason why one of these 'systems' could not be the 'surroundings'.

The word *spontaneous* mentioned above refers to a change not needing to be driven by work. The flow of energy from a hot reservoir to a cold reservoir in the form of heat is a spontaneous change. A particular manifestation of the **second law** is that:

The entropy of the universe (system plus surrounding) increases in the course of any spontaneous change.

CHAPTER 8: ENTROPY

Example question: Explain how the cooling of a hot cup of coffee increases the entropy of the universe.

Solution: The coffee cools by heat transfer, its entropy *decreases*. Similarly, as heat is transferred into the room, its entropy *increases*. Here is the crucial point: the amount by which the room's entropy increases is greater than the amount by which the coffee's entropy decreases. The result as far as the 'universe' is concerned is that the total entropy contained in the 'universe' has increased.

Example question: Explain how the entropy of the stellar universe increases.

Solution: Let body (1) represents all the stars in the universe, and body (2) represents the vacuum of space. Body (1) is a heat source at several thousand degrees Kelvin. The microwave background radiation is at about 3K. $T_1 \gg T_2$ and the entropy of the universe is increasing. Eventually (depending on whose cosmological model you believe!), the entropy of the universe will reach a maximum—this corresponds to an equilibrium UNIFORM temperature for the whole universe. Although energy has been conserved during the evolution of the universe, its quality has degraded to the point where it can no longer drive processes such as stellar nucleosynthesis, gravitational clumping of matter, planet formation or life. This final end state is called the **heat death**.

APPENDIX: Additional examples to understand entropy and 2nd law

The Second Law Revisited

The second law of thermodynamics is one of the most fundamental laws of nature, having profound implications. In essence, it says this:

The second law - The level of disorder in the universe is steadily increasing. Systems tend to move from ordered behaviour to more random behaviour.

One implication of the second law is that heat flows spontaneously from a hotter region to a cooler region, but will not flow spontaneously the other way. This applies to anything that flows: it will naturally flow downhill rather than uphill.

If you watched a film forwards and backwards, you would almost certainly be able to tell which way was which because of the way things happen. A pendulum will gradually lose energy and come to a stop, but it does not pick up energy spontaneously; an ice cube melts to form a puddle, but a puddle never spontaneously transforms itself into an ice cube; a glass falling off a table might shatter when it hits the ground, but the pieces will never spontaneously jump back together to form the glass again. Many processes are irreversible, and any irreversible process increases the level of disorder. One of the most important implications of the second law is that it indicates which way time goes - time naturally flows in a way that increases disorder.

The second law also predicts the end of the universe: it implies that the universe will end in a "heat death" in which everything is at the same temperature. This is the ultimate level of disorder; if everything is at the same temperature, no work can be done, and all the energy will end up as the random motion of atoms and molecules.

<u>Entropy</u>

We mentioned earlier that a measure of the level of disorder of a system is entropy. Although it is difficult to measure the total entropy of a system, it is generally fairly easy to measure changes in entropy using some of the equations covered in this chapter.

The second law of thermodynamics can be stated in terms of entropy. If a reversible process occurs, there is no net change in entropy. In an irreversible process, entropy always increases, so the change in entropy is positive. The total entropy of the universe is continually increasing.

There is a strong connection between probability and entropy. This applies to thermodynamic systems like a gas in a box as well as to tossing coins. We will look at these 2 examples in more detail below.

Example1: Gas in a box

With a gas in a box, the probability that all the gas molecules are in one corner of the box at the same time is very small (for a typical box full of 10^{20} molecules or more, incredibly small); this is therefore a low entropy state. It is much more likely that the molecules are randomly distributed around the box, and are moving in random directions; this high disorder state is a considerably higher entropy state. The second law does not rule out all the molecules ending up in one corner, but it means it is far more likely that the molecules will be randomly distributed, and to move towards a random distribution from an orderly distribution, as opposed to the other way around.

Example2: Tossing a coin

If you have four pennies, for example, the likelihood that all four will land heads up is relatively small. It is six times more likely that you will get two heads and two tails. The two heads - two tails state is the most likely, shows the most disorder, and has the highest entropy. Four heads is less likely, has the most order, and the lowest entropy. If you tossed more coins, it would be even less likely that they would all land heads up, and even more likely that you would end up with close to the same number of heads as tails.

Tutorial Questions

Calculation of entropy

- (a) When the water has reached 100°C what has been:
 - (i) the change of entropy of the water; [+13.065kJ/K]
 - (ii) the change of entropy of the reservoir; [-11.223kJ/K]
 - (iii) the change of entropy of the universe? [+1.842kJ/K]
- (b) If the water had been heated from 0°C to 100°C by first bringing it into contact with a reservoir at 30°C and then a reservoir of 100°C, what would have been the change in the entropy of the universe? [+1.065kJ/K]
- (c) Explain how the water could have been heated to give no change in the entropy of the universe. [Use an infinite number of reservoirs, so that $\Delta T \rightarrow 0$]
- 2. A system contains a fluid at a temperature of 70°C and 1 bar. It undergoes a reversible process during which the temperature of the system remains constant. Given that the heat transfer to the fluid during the process is 100 kJ. evaluate:
 - (i) The increase in entropy. [0.292kJ/K]

If the system has a mass of 2.31 kg;

- (ii) Evaluate the increase in specific entropy of the system. [126.2J/kgK]
- (iii) If a second fluid system, identical to the first one undergoes an irreversible isothermal process from the same initial state to the same final state as above; and the heat transfer to the fluid in this irreversible process is 80 kJ; evaluate the increase in entropy of the fluid. [trick question: same answer as (ii)]
- 3. Calculate the gain in entropy when 1 kg of water at 30°C is converted into steam at 150°C and then superheated to 300°C, with the process taking place at constant pressure. Take $c_{p(water)} = 4.2 \text{ kJ/kg}$

K, $c_{p(steam)} = 2.1 \text{ kJ/kg K}, h_{fg} [kJ/kg] = 2340 - 1.5 t$, where t = temperature in °C. [7.039 kJ/kgK]

Isentropic expansion of steam (use tables)

- 4. Superheated steam at 10 bar and 250°C expands isentropically to 1 bar. Find the final condition. [*p*=1 bar, *x*=0.929]
- 5. This question compares the effects of performing a process in a constant volume (closed) or constant pressure (open) system
 - (i) A cylinder contains 1 kg of steam at 6 bar and dryness is 0.9. The piston is moved so that the steam expands reversibly and adiabatically until the pressure becomes 1 bar. Determine the work done on the piston. [245kJ/kg]
 - (ii) Steam flows steadily through a turbine. At entry the pressure is 6 bar and dryness is 0.9 and the exhaust pressure is 1 bar. Determine the work done per kg of steam flow assuming reversible adiabatic expansion. [276.4kJ/kg]
- 6. A cylinder contains 0.015 m³ of dry saturated steam at 8 bar. The steam expands reversibly and adiabatically until the pressure becomes 0.8 bar. Determine the final volume and the work done by the steam during the expansion. [0.114 m³, 21.25 kJ]

- 7. Steam flows steadily through a throttle valve. On the upstream side of the valve the pressure is 17 bar and the dryness is 0.95 while on the downstream side the pressure is 13 bar. The steam then flows through a turbine with exhaust pressure of 0.14 bar. Determine the percentage reduction in turbine output due to the throttling of the steam which has occurred in the valve. Assume the expansion in the turbine is isentropic. [5% reduction]
- 8. Wet steam flowing steadily along a pipe at 20 bar is throttled to 7 bar before being expanded isentropically in a nozzle. The temperature before the nozzle is 175°C and the back pressure is 0.2 bar. Determine the exit velocity of the steam from the nozzle. Determine also the exit velocity if no throttling had occurred before the nozzle. [1005 m/s, 1190 m/s]