Chemical Thermodynamics at a Glance

H. DONALD BROOKE JENKINS

Blackwell Publishing

Chemical Thermodynamics at a Glance

H. Donald Brooke Jenkins

Professor of Chemistry, Department of Chemistry
University of Warwick, Coventry
UK

Blackwell
Publishing

© 2008 H. Donald Brooke Jenkins

Blackwell Publishing editorial offices:
Blackwell Publishing Ltd, 9600 Garsington Road, Oxford OX4 2DQ, UK
Tel:+44 (0)1865 776868
Blackwell Publishing Inc., 350 Main Street, Malden, MA 02148-5020, USA
Tel:+1 781 388 8250
Blackwell Publishing Asia Pty Ltd, 550 Swanston Street, Carlton, Victoria 3053, Australia
Tel:+61 (0)3 8359 1011

The right of the Author to be identified as the Author of this Work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book.

This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

First published 2008 by Blackwell Publishing Ltd

ISBN: 978-1-4051-3997-7

Library of Congress Cataloging-in-Publication Data

Jenkins, H. Donald Brooke.
Chemical thermodynamics at a glance / H. Donald Brooke Jenkins. – 1st ed.
p. cm. – (Chemistry at a glance)
Includes index.
ISBN-13: 978-1-4051-3997-7 (pbk. : alk. paper)
ISBN-10: 1-4051-3997-8 (pbk. : alk. paper) 1. Thermodynamics. 2. Chemical equilibrium. 3. Entropy. 4. Thermochemistry I. Title.

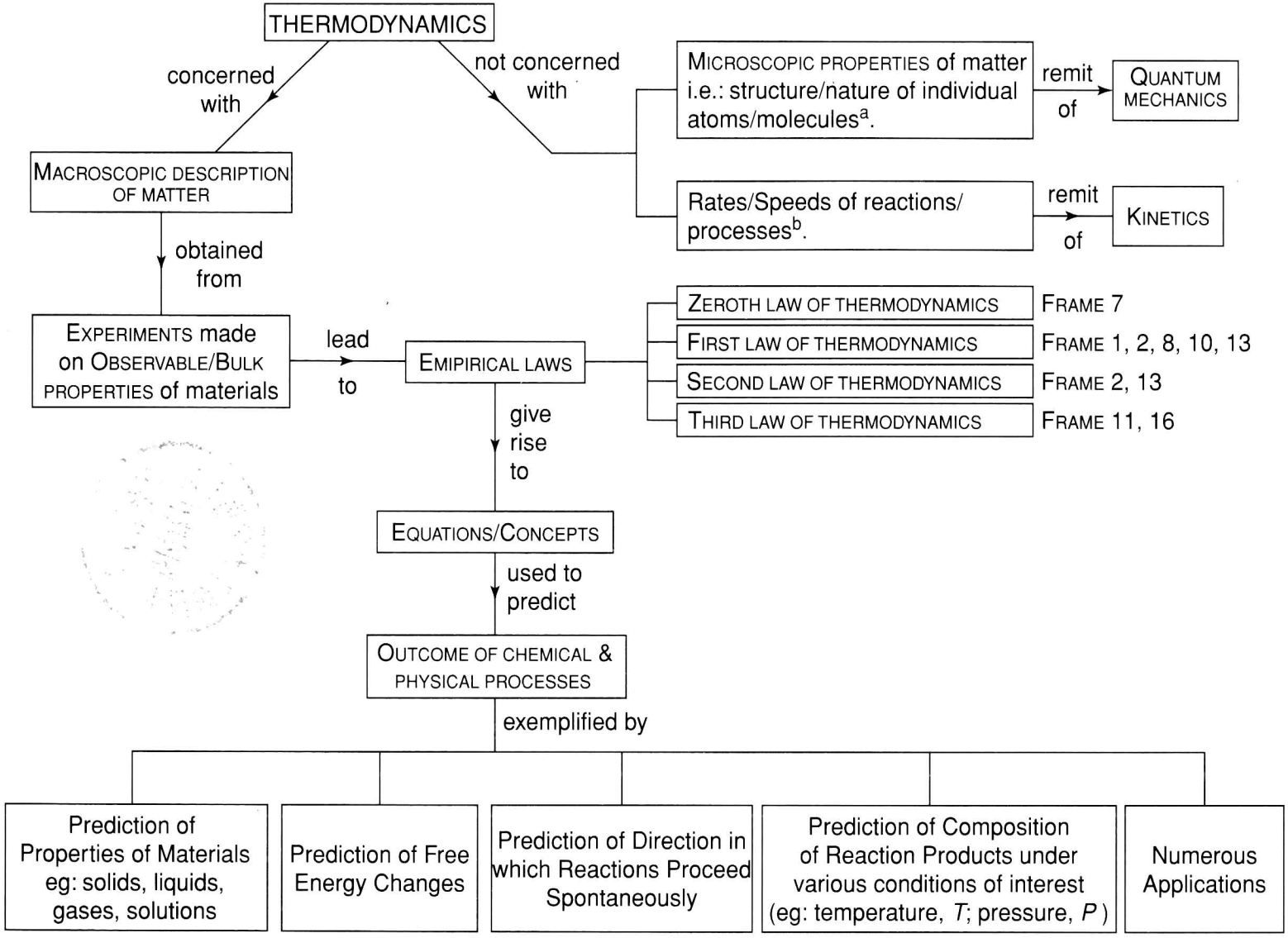
QD504.J46 2007
541′.369 – dc22 2007007114

A catalogue record for this title is available from the British Library

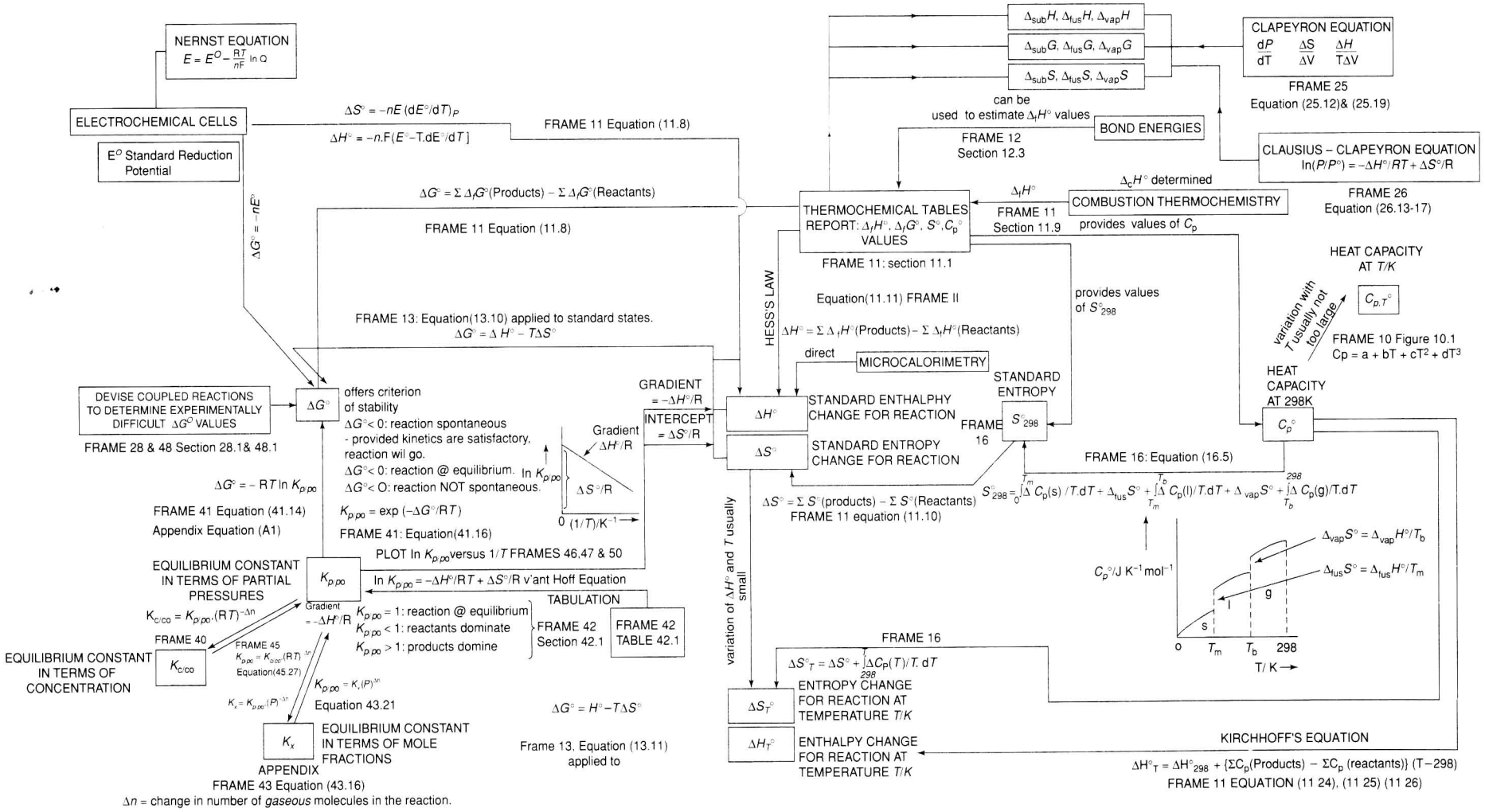
Set in 9.5/11.5 Times by Aptara Inc., New Delhi, India
Printed and bound in Singapore
by Utopia Press Pte Ltd

The publisher's policy is to use permanent paper from mills that operate a sustainable forestry policy, and which has been manufactured from pulp processed using acid-free and elementary chlorine-free practices. Furthermore, the publisher ensures that the text paper and cover board used have met acceptable environmental accreditation standards.

For further information on Blackwell Publishing, visit our website:
www.blackwellpublishing.com



Frame 7 The evolution, nature and limitations of thermodynamics. See Note 7.1.



Frame 54 Core thermodynamic relationship.

此为试读，需要完整PDF请访问：www.ertongbook.com

To my colleagues at universities here and abroad who give their friendship and to my numerous students, past and present, who are always a source of delight.

To Sheila Anne Jenkins.

Preface

When Blackwell approached me about writing this book I was pleased to respond. With many decades of experience in teaching thermodynamics and with an understanding of the need to present the underlying mathematics needed in a palatable way, I felt up to the challenge. Armed with the results of Blackwell's own suvey of both UK and American universities' teaching needs in this area the contents seemed pretty self-evident.

Students these days come to university armed with a very varied and often quite novel range of experience and this enforces the need to present difficult subjects like thermodynamics in a logical (but, at the same time, quite thorough) way.

Such is the aim of this text. Thermodynamics and the necessary mathematics are embodied as a series of 54 'Frames' plus an Appendix. These frames are multicrossreferenced which enables the text to be used in a variety of ways:

- as a means of reading up on thermodynamics and using the 'bite-sized' frames as the basis of one hour study periods which develop in a logical and progressive manner and cover the necessary thermodynamics for most undergraduate science courses.
- as an aide memoire to review course material already received. In this mode one can start reading at any Frame and because these are liberally cross-referenced the reader will be directed to different sections of the book according to need;
- as a last minute revision aid for examinations, to review specific parts of the syllabus quickly and easily. The extensive index to the frames provides an immediate location of the relevant Frames needed to highlight a given topic. The division of the material into short sections makes this much easier than ploughing through the standard text. The use of bullet points is intended to further clarify the important points. The overview presented in Frame 54, and the figure printed inside the front cover of the book will also be found useful;
- The book can also be used at the post-graduate level to supplement, refresh and reinforce earlier teaching.

I have tried to contain within the 54 Frames presented, sufficient discussion of the necessary maths, as well as of the relevant thermodynamics suitable for an undergraduate course (such as is provided here at Warwick).

The author has drawn widely on his accumulated knowledge acquired by reading the many texts (too numerous to mention) available in thermodynamics and it is from the authors of such texts that many of the ideas presented have their origins and to whom thanks are due. Also there is a degree of originality built into many of the Frames that attempts to present some of the more difficult material in a new light.

The author, as well as being an acclaimed teacher, is also an active researcher who has recently developed a new approach to thermodynamics (VBT – Volume Based Thermodynamics) published in high impact international journals, which is proving useful as a research tool.

The author has recently reported an entirely new approach for the acquisition of thermochemical data for condensed materials. The author lectures widely in this country and abroad.

I am indebteded to my colleague Dr Joe Lee (University of Manchester) who gave of his time willingly and diligently in order to read the manuscript of this text and make the many useful and improving comments he did. His insightfulness led to many interesting and stimulating phonecalls and I am grateful to him both as a personal friend and as one of my former teachers. Naturally any errors that may remain are totally my responsibility. I also acknowledge the constant help and support given to me by Sheila Anne Jenkins in all of my projects, not least, in the preparation of the manuscript for this book.

I hope that you may find this text useful and I would be glad to hear from students, worldwide, about their experiences with the text in the hope that any future edition can reflect on these and improve presentation whenever necessary.

Contents

Preface		vii
0	Symbols and Notation	1
1	Thermodynamic Changes, Properties and Types of Function	4
2	Integration in Thermodynamics	8
3	Graphical Gradients and Intercepts	12
4	The Ideal Gas	16
5	Partial Derivatives $(\partial Z/\partial Y)_x$ Simplified	18
6	Logarithms and Exponentials	20
7	Thermodynamics Conventions	24
8	Heat and Work. First Law of Thermodynamics	26
9	Work of Expansion	28
10	Internal Energy, U and Enthalpy, H	30
11	Reference States	34
12	Bond Enthalpy (Energy)	38
13	Spontaneity, Entropy and Gibbs Energy	40
14	Entropy and Second Law	44
15	Calculation of Entropy	48
16	The Third Law of Thermodynamics	52
17	The Statistical Definition of Entropy	54
18	Variation of G with T $(\mathrm{d}P = 0)$	56
19	Variation of H and S with T $(\mathrm{d}P = 0)$	58
20	Variation of G and S with P $(\mathrm{d}P = 0)$	60
21	Variation of G with T for Solid, Liquid and Gaseous Phase	64
22	Variation of H with T for Solid, Liquid and Gaseous Phase	66
23	Effect of Pressure on Melting Point and Boiling Point: Normal Substances	68
24	Effect of Pressure on Melting Point and Boiling Point: Water	72
25	Phase Equilibria. Clapeyron Equation	74
26	Clausius–Clapeyron Equation	76
27	Open Systems. Chemical Potential. Chemical Reactions	78
28	Coupled Reactions	82
29	Chemical Potentials Applied to Physical Processes	84
30	The Phase Rule	88
31	Ideal and Real Gases. Dalton's Law of Partial Pressures	92
32	Ideal Liquid Mixtures. Vapour Pressure and Raoult's Law	94
33	Ideal Liquid Mixtures. Real Liquid Mixtures	98
34	Binary Liquid Mixtures	102
35	Chemical Potentials and Equilibrium Relationships	106
36	Interpretation of Logarithmic Term. Molality	110
37	Thermodynamics of Ideal Mixing	116
38	Chemical Potentials of Real Gases. Fugacity	122
39	Chemical Potentials of Real Solutions. Activity	126
40	Measurements of Equilibrium Constant, K	132
41	Reaction Quotient, Q and Equilibrium Constant, K. Relationship Between ΔG^o and K_{p/p^o}	134
42	Chemical Equilibrium	136
43	K for a Multiphase Reaction	138
44	Reactions *Not* at Equilibrium	142
45	Equilibrium Calculations for Reactions *Not* Initially at Equilibrium	146
46	Gibbs–Helmholtz Equation	150
47	Qualitative Interpretation of Van't Hoff Equation. Coupled Reaction	154
48	Variation of Equilibrium Constant, K, with Overall Total Pressure, P	158
49	Le Chatelier's Principle	160
50	Gibbs–Duhem Equation	164
51	Colligative Properties: Freezing Point	168

52 Colligative Properties: Boiling Point 174
53 Colligative Properties: Osmotic Pressure, Π 176
54 Core Thermodynamic Relationships 178
Appendix A: The Logarithmic Function in Thermodynamics 179
Notes 186

Index 193

0. Symbols and Notation

Thermodynamics employs quite complicated notation which, at first sight, may give the impression of great difficulty. This can be totally misleading and should not be allowed to discourage beginners. In actual fact the notation is intended to make things *easier* to understand in most cases.

Thus, in this text, several pre-amble frames are first presented which explain areas where experience of teaching has shown students have uncertainties or difficulties. The key is to read these frames carefully and to become familiar with the meaning, not forgetting to employ the extensive cross-referencing between the various frames to supplement your knowledge.

The purpose of the tables below is:

- To give the IUPAC standard notation for symbols which are commonly abbreviated to rather more simple notation in this text.
- These abbreviations were consciously made in order that the text did not become cluttered with extended symbols and terminology. To have retained the suggested notation, on the grounds of rigour, would have led to a text that might have appeared to be more complicated than it is. So the form presented is to give, in the table below, details of the IUPAC notation and alongside this give a compendium of symbols used in the text. Cross-reference can then be made at will (see also *Quantities, Units and Symbols in Physical Chemistry*, I. Mills, Blackwell Scientific Publications (latest edition), for the definitive word on this issue).

In most cases the properties refer to one mole of material or one mole of reactant.

Table 0.1 Symbols, terminology and units.

Symbol	Quantity	Usual units	Notes	IUPAC symbol
A	Helmholtz energy	kJ mol^{-1}	$A = U - TS$	$\boldsymbol{A}$
A	area of a triangle	m^2	$A = {}^1/_2$(base)(perpendicular height)	$\boldsymbol{A}$
a	activity			$\boldsymbol{a}$
$a_\pm$	mean ionic activity		$a_\pm = m_\pm \cdot \gamma_\pm / m^o$	$a_\pm$
C_p	heat capacity at constant pressure	J K^{-1} mol^{-1}	$C_p = (\partial H/\partial T)_P$	$\boldsymbol{C_{p,m}}$
C_v	heat capacity at constant volume	J K^{-1} mol^{-1}	$C_V = (\partial U/\partial T)_V$	$\boldsymbol{C_{v,m}}$
$[\ ] = c$	amount, molar concentration	mol dm^{-3}	used in equilibrium expressions	
$[\ ]_o = c^o$	standard molar concentration	mol dm^{-3}	used in equilibrium expressions	
$[H^+] = 10^{-7}$	biochemical standard state	mol dm^{-3}	denoted by prime on symbol e.g. $\Delta G^{o'}$	$\boldsymbol{\Delta_r G^o}$
ρ	density, mass density	g cm^{-3}		$\boldsymbol{\rho}$
e	charge on the proton	C	$e = 1.602 \times 10^{-19}$ C	
EA	electron affinity	kJ mol^{-1}	$X(g) + e^-(g) \rightarrow X^-(g)$	
f	fugacity	Pa	effective pressure of real gases	$\boldsymbol{f}$
F	Faraday constant	C mol^{-1}	$F = eL = 96{,}485.3$ C mol^{-1}	$\boldsymbol{F}$
G	Gibbs energy (Gibbs free energy)	kJ mol^{-1}	$G = H - TS$	$\boldsymbol{G_m}$
γ	activity coefficient		$= a/x = a/m_i$ (species i)	$\boldsymbol{\gamma}$
$\gamma_\pm$	mean ionic activity coefficient		$\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-}$	$\boldsymbol{\gamma_\pm}$
H	enthalpy	kJ mol^{-1}	$H = U + PV$	
IP	ionisation potential	kJ mol^{-1}	$M(g) \rightarrow M^+(g) + e$	
K_a	equilibrium constant written in terms of activity	dimensionless		$\boldsymbol{K_a}$
$K_{c/co}$	equilibrium constant written in terms of concentration ratios: $[\ ]/[\ ]_o$	dimensionless		$\boldsymbol{K_{c/co}}$
$K_{p/po}$	equilibrium constant written in terms of partial pressure ratios: p/P^o	dimensionless	$\Delta G^o = -RT \ln K_p$	$\boldsymbol{K_{p/po}}$
$K_{m/mo}$	equilibrium constant written in terms of partial pressure ratios: p/P^o	dimensionless		$\boldsymbol{K_{m/mo}}$
subscript m	implies molar quantity (m can be omitted since units can indicate molar quantity (e.g. mol^{-1}))			e.g. $\boldsymbol{\Delta_{vap} H_m}$
subscript r	implies reaction (also implies molar)			e.g. $\boldsymbol{\Delta_r G^o}$, $\boldsymbol{\Delta_r H^o}$
μ	chemical potential	J mol^{-1}	$(\partial G/\partial n_B)_{T,\,P,\,nj \neq nB}$	$\boldsymbol{\mu}$
m	mass	kg		$\boldsymbol{m}$
$m_\pm$	mean ionic molality	mol kg^{-1}	$m_\pm^{(\nu_+ + \nu_-)} = m_+^{\nu_+} \cdot m_-^{\nu_-}$	$\boldsymbol{m_\pm}$
m	molarity	mol kg^{-1}		$\boldsymbol{m}$
L, N_A	Avogadro constant	mol^{-1}	$= 6.023 \times 10^{23}$	$\boldsymbol{L}$, $\boldsymbol{N_A}$
n	amount (of substance)	dimensionless		$\boldsymbol{n}$

(continued)

Table 0.1 (*continued*)

Symbol	Quantity	Usual units	Notes	IUPAC symbol
P	total pressure 1 bar = 100 kPa = 10^5 Pa; 1 mmHg = 1 Torr; 1 atm = 760 Torr = 101325 Pa; 1 bar = 10^5 Pa	Pa / bar	$P = \sum p_i = (RT/V)\sum n_i$	$\boldsymbol{P}$
p_i	partial pressure of gas i in mixture	Pa / bar / atm		$\boldsymbol{p_i}$
q	heat absorbed by thermodynamic system from surroundings	J (kJ)	acquisitive convention	$\boldsymbol{q}$
q_P	heat absorbed by thermodynamic system at constant pressure from surroundings	J (kJ)		$\boldsymbol{q_P}$
q_V	heat absorbed by thermodynamic system at constant volume from surroundings	J (kJ)		$\boldsymbol{q_V}$
R	gas constant	J K^{-1} mol^{-1}	= 8.314 J K^{-1} mol^{-1}	$\boldsymbol{R}$
S	entropy	J K^{-1} mol^{-1}		$\boldsymbol{S}$
T	temperature	K		$\boldsymbol{T}$
T_b	boiling point	K		
T_f	fusion temperature	K		
T_m	melting point	K		
T_{sub}	sublimation temperature	K		
$U(=E)$	internal energy	kJ mol^{-1}	denoted E in some textbooks	$\boldsymbol{U}$
V	volume	m^3		$\boldsymbol{V}$
V_m	molar volume	m^3		$\boldsymbol{V_m}$
w	work done by surroundings on system	J (kJ)	uses acquisitive convention	$\boldsymbol{w}$
w'	work done other than (PV) mechanical work of expansion/compression done by surroundings on system	J (kJ)	uses acquisitive convention e.g. gravitational, electrical work etc.	$\boldsymbol{w'}$
x_i	mole fraction of component i	dimensionless		$\boldsymbol{x_i}$
X_f	final value of property X (state function) following a change	units of X		
X_i	initial value of property X (state function) before a change	units of X		
$\Delta_f G^o$	standard Gibbs energy of formation per mole	kJ mol^{-1}		$\boldsymbol{\Delta_f G^o}$
ΔH^o	enthalpy change per mole under standard conditions			$\boldsymbol{\Delta_r H}$
$\Delta H^o(X–Y)$	bond enthalpy or bond dissociation enthalpy for X–Y bond sometimes written as E(X–Y) or BE(X–Y) and (wrongly) described as bond *energy*			
$\Delta_{at} H^o$	standard enthalpy of atomisation per mole (compound (s, l, g) → atom(g)			
$\Delta_c H^o$	standard enthalpy of combustion per mole (compound + O_2(g) → CO_2(g) + H_2O(l) + etc)			$\boldsymbol{\Delta_c H^o}$
$\Delta_f H^o$	standard enthalpy of formation per mole (elements in standard states →compound)			$\boldsymbol{\Delta_f H^o}$
$\Delta_{fus} H^o$	standard enthalpy of fusion per mole (solid → liquid)			$\boldsymbol{\Delta_{fus} H}$
$\Delta_{hyd} H^o$	standard enthalpy of hydration (ion(g) → ion(aq))			$\boldsymbol{\Delta_{hyd} H^o}$
$\Delta_{mix} H^o$	standard enthalpy of mixing per mole (ion(g) → ion(aq))			$\boldsymbol{\Delta_{mix} H^o}$
$\Delta_r H^o$	standard enthalpy of reaction per mole (reactants → products)			$\boldsymbol{\Delta_r H^o}$
$\Delta_{sub} H^o$	standard enthalpy of sublimation per mole (solid → gas)			$\boldsymbol{\Delta_{sub} H^o}$
$\Delta_{sol} H^o$	standard enthalpy of solution per mole (solute → solution)			$\boldsymbol{\Delta_{sol} H^o}$
$\Delta_{trs} H^o$	standard enthalpy of transition per mole (between phases)			$\boldsymbol{\Delta_{trs} H^o}$
$\Delta_{vap} H^o$	standard enthalpy of vaporisation per mole (liquid → gas)			$\boldsymbol{\Delta_{vap} H^o}$
$\Delta_f S^o$	standard entropy of formation per mole			$\boldsymbol{\Delta_f S^o}$
ΔU	internal energy change per mole sometimes written as ΔE [ΔU = w (adiabatic process, q = 0); ΔU = 0 (*isolated system*); $\Delta U = q + w$ (*open* system); $\Delta U = q$ (closed system, dV = 0)]			$\boldsymbol{\Delta_U}$

此为试读,需要完整PDF请访问: www.ertongbook.com

Table 0.2 Notation used to denote changes in thermodynamic properties.

Notation	Meaning	Notes
δq, δw	infinitesimally small *quantities* of heat added to system or work done by surroundings on system	'delta' q or w only defined for process or path *not* changes in state functions
dX	small *change* in property X (state function)	'dee' X (e.g. dU)
ΔX	measurable *change* in property X (state function)	'Delta' X N.B. changes: $\delta \ll d < \Delta$
$dX \rightarrow 0$	change in X approaches zero	
dy/dx	differential coefficient of y with respect to x	
$dV = 0$	no change in volume	isochoric process
$dP = 0$	no change in pressure	isobaric process
$dT = 0$	no change in temperature	isochoric process
$\delta q = 0$	no heat enters or leaves system	adiabatic process
$\int$y.dx	integral of y with respect to x	
$\sum$	sum of individual values	e.g. $\sum_{i=1}^{3} x_i = x_1 + x_2 + x_3$
$\prod$	product of individual values	e.g. $\prod_{i=1}^{3} x_i = x_1.x_2.x_3$
$\sum \Delta_f X^o$(Products)	sum of individual $\Delta_f X^o$ values ($X = G$ or H) of all products of a reaction	
$\sum \Delta_f X^o$(Reactants)	sum of individual $\Delta_f X^o$ values ($X = G$ or H) of all reactants of a reaction	
$N!$	$= N(N-1)(N-2)(N-3)....3.2.1$	'factorial N' e.g. $6! = 6.5.4.3.2.1 = 720$
0!	factorial zero	$= 1$
|x|	modulus of x	i.e. positive value of x (ignores any negative sign)
$>$	greater than	e.g. $8 > 6$
$\geq$	greater than or equal to	
$<$	less than	e.g. $4 < 7$
$\leq$	less than or equal to	
$\pm$	plus or minus	
$\neq$	not equal to	e.g. $4 \neq 5$
$\approx$	approximately equal to	
$\int$	integral of	
a ± b ± c	means a + b + c (upper signs) and a − b − c (lower signs)	used for shorthand form of equations
(s) or (c)	solid or crystalline phase	e.g. H_2O(s) = ice
(l)	liquid phase	e.g. H_2O(l) = water
(g)	gaseous (vapour) phase	e.g. H_2O(g) = steam
^{o}	standard state (superscript)	sometimes written as $^{\ominus}$
$_o$	standard state (subscript)	e.g. $[\ ]_o$ standard state concentration
ΔC_p^o	$= \sum C_p$(Reactants) − $\sum C_p$(Products) for a reaction	
$\Delta_f G^o$	standard Gibbs energy of formation per mole	
ΔH^o	enthalpy change per mole under standard conditions	
$\Delta H^o(X-Y)$	bond enthalpy or bond dissociation enthalpy for X–Y bond sometimes written as E(X – Y) or BE(X – Y) and (wrongly) described as bond *energy*	

1. Thermodynamic Changes, Properties and Types of Function

1.1 Thermodynamic System and Surroundings

A thermodynamic *system* refers to:

the physical process or the chemical reaction at the centre of interest.

The remainder of the universe is designated to be:

the surroundings, although in practice, these can be restricted to those parts of the universe adjacent to the system.

One can define the boundaries of the thermodynamic system in any way one chooses.

Systems can be classified (see Figure 7.3, Frame 7) as follows:

CLOSED SYSTEM – no material is exchanged with the surroundings (e.g. autoclave – a sealed vessel for carrying out high pressure reactions).
OPEN SYSTEM – material is exchanged (e.g. by evaporation) with the surroundings. The system does not have to be OPEN in order to change the amounts of substances present; this can occur by chemical reaction or interphase transfer within a closed system.
ISOLATED SYSTEM – neither material nor energy exchange with the surroundings (e.g. thermos flask).

Processes can be either:

CHEMICAL – involving reaction and chemical change or PHYSICAL – involving physical change (e.g. variation of pressure, P, or phase such as in boiling (liquid $\rightarrow$ vapour).

Many processes involve one or more of the following situations (d denotes a change in the property specified):

ISOTHERMAL = constant temperature ($\mathrm{d}T = 0$);
ISOCHORIC = constant volume ($\mathrm{d}V = 0$);
ISOBARIC = *Isopiestic* = constant pressure ($\mathrm{d}P = 0$);
ADIABATIC = no flow of heat ($q = 0$) between system and surroundings;
REVERSIBLE = process in which certain parameters (usually pressure, P or temperature, T) are only minutely (i.e. infinitesimally) different from those of the immediate surroundings. The process must also be close to equilibrium;

Energy can be transferred between the surroundings and the system and is subdivided into:

heat, represented by the symbol, q and work, represented by the symbol, w.

Work can be further subdivided into various categories: mechanical or 'PV' work (Frames 8 and 9), $w = -P\mathrm{d}V$; electrical work, $w_{\mathrm{elec,}}$ (see Equation (8.13), Frame 8); magnetic work, w_{mag}; gravitational work, w_{grav} (see Equation (8.12), Frame 8); surface work, w_{surf} etc.

1.2 Thermodynamic Changes

A property, X, which *alters its value* from an *initial state* (i) (value of the property X_{i}) to a *final state* (f) (value of the property X_{f}) has changed in value by $(X_{\mathrm{f}} - X_{\mathrm{i}})$. If change occurring in X is *small*, we denote this by $\mathrm{d}X$ and for *larger* (measurable) changes, by ΔX. Such notation applies predominantly to *state functions* (see section 1.7 below), examples are H (enthalpy), U (internal energy), G (Gibbs energy), etc.

To talk about a *change*, $\mathrm{d}q$, in *heat added* to a thermodynamic system and to try and equate it to $(q_{\mathrm{f}} - q_{\mathrm{i}})$ does not make any sense since it is impossible to define, or quantify, the *amount of heat possessed* by a body (or contained within it) at any 'snapshot' instant. Therefore q_{i} and q_{f} are simply *not definable* for a process in the same way that we can record the temperature, T, at any instant. Hence q is *not* a property of a system but is defined only *during a change* – we can only measure *quantities* of heat *supplied* or *released* during a process. Addition (or release) of an infinitesmally small *amount* of heat is denoted by δq.

Similarly work done, w, *by* or *on* a system, (Frames 8 and 9), a *quantity of work* is either *attributable to* or *transferred* during a physical change (e.g. during expansion or contraction); but there is no amount of work *possessed* by a system at any instant, it is definable only during a process.

Thus q and w are different from most other functions in thermodynamics.

1.3 Thermodynamic Intensive and Extensive Properties

Thermodynamic properties which depend on the *amount (mass) of material present* (e.g. internal energy: U; enthalpy: H, etc.) are termed EXTENSIVE properties.

For *extensive* quantities, X (in general):

$$X_m = \text{molar } X = \overset{\text{definition}}{\frac{X}{n}} \tag{1.1}$$

where n is the amount of material present. Since X is proportional to n, the above quotient in (1.1) is independent of n and therefore X_m is INTENSIVE.

Intensive properties are such that if the material were continuously sub-divided then the property would be *identical for all parts* of the sub-divided material. Such properties are independent of the size (or amount) of sample (e.g. density: ρ; temperature: T and all molar quantities. Frequently in the text we omit the subscript m from the symbol.

Extensive quantities show an *exact* proportionality to n, only when intensive quantities, like T and P, remain constant.

1.4 Molar Quantities and the Concept of the Mole

Molar as an adjective does *not* actually mean 'of or for 1 mole'. For a pure substance molar means simply 'divided by amount of substance'. Thus the molar mass of material, M, is the mass of the material, w divided by the amount of material, n:

$$M = \frac{w}{n} \tag{1.2}$$

Since the purpose of this book is presentation of thermodynamics in a form which is easy to assimilate the use of IUPAC (the body recommending chemical notation) notation has *not* been adopted in the text, but *importantly*:

reference to IUPAC notation is provided in the glossary (Frame 0).

Thus use of extended symbols (e.g. $C_{p,m}$ $\Delta_m H$) has usually been avoided. The simpler forms C_p and ΔH being adopted.

IUPAC recommend that the *mole* should be replaced by amount of substance. Readers should however be aware of the wide usage of the concept of the mole elsewhere. The term *mole fraction*, x, is a IUPAC acceptable name. The Term *amount fraction* is not recommended.

1.5 Meaning of the Term *Molar* in Relation to Chemical Reactions

Consider the combustion reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \tag{1.3}$$

at 298K and 1 bar (= 100 kPa).

Molar enthalpy of combustion of methane gas, $\Delta_c H^o(CH_4, g)$

If the amount of methane gas combusted is $n(CH_4)$ and the enthalpy change on combustion is ΔH, then the molar enthalpy of combustion is given by:

$$\Delta_m H = \Delta_c H^o(CH_4, g) = \frac{\Delta H}{[n(CH_4, g)\,\text{combusted}]} = \frac{\Delta H}{[-\Delta n_{CH4}]} = \Delta H \tag{1.4}$$

where Δn_{CH4} is the change in the amount of methane (since methane decreases, this quantity will be negative (= −1 mol). Thus $-\Delta n_{CH4}$ is then positive.

On the other hand where there is no intention to focus on any one particular species we treat things differently:

1.5.1 Molar enthalpy (change) of the reaction (1.3)

The molar enthalpy change of the reaction is calculated using the equation:

$$\Delta_m H = \frac{\Delta H}{\Delta \xi} \tag{1.5}$$

where $\Delta\xi$ (delta xi) is the change in the extent of the reaction.

The reaction (1.3) above is a statement of the stoichiometry, and reports the *stoichiometric* numbers, v, which take values:

$$v_{CH4} = -1; \quad v_{O_2} = -2; \quad v_{CO_2} = +1; \quad v_{H_2O} = +2; \tag{1.6}$$

recorded as: positive (+) for products, and negative (−) for reactants.

Suppose that we undertake combustion of 16 g (i.e. 1 mol) methane gas at a particular temperature, T and pressure, P and determine, calorimetrically, the change in enthalpy, ΔH (in units of J or kJ). We define:

$$\begin{aligned} \Delta n_{CH_4} &= \{[\text{amount of } CH_4 \text{ in products}] - [\text{amount of } CH_4 \text{ in reactants}]\} \\ &= (0 - 1)\,\text{mol} = -1\,\text{mol} \end{aligned} \tag{1.7}$$

similarly:

$$\Delta n_{O_2} = (0 - 2) = -2\,\text{mol}; \Delta n_{CO_2} = (1 - 0) = +1\,\text{mol}; \Delta n_{H_2O} = +2\,\text{mol} \tag{1.8}$$

[In equations (1.7)–(1.8) a negative sign signifies overall *loss* (of reactant); a positive sign signifies an overall *gain* (of product)].

The extent of our experimental reaction, $\Delta\xi$ (the same for all species involved) can be calculated using:

$$\Delta\xi = \Delta n_{CH4}/v_{CH4} = \frac{(-1)}{(-1)} = 1\,\text{mol} \tag{1.9}$$

similarly:

$$\Delta\xi = \Delta n_{O_2}/v_{O_2} = \frac{(-2)}{(-2)} = 1\,\text{mol}; \Delta\xi = \Delta n_{CO_2}/v_{CO_2} = \frac{(+1)}{(+1)} = 1\,\text{mol}; \Delta\xi = \Delta n_{H_2O}/v_{H_2O} = \frac{(+2)}{(+2)} = 1\,\text{mol} \tag{1.10}$$

thus:

if we combust 1 mol of methane this will correspond to 1 *mole of reaction* (or, $\Delta\xi$ is 1 mol).

Now $\Delta_m H$, the *molar* enthalpy change of the combustion reaction, is given as:

$$\Delta_m H = \frac{\Delta H}{\Delta\xi} = \Delta H \tag{1.11}$$

BUT if the chemical equation (1.3) given is multiplied through by a factor of $^1/_2$ to give:

$$^1/_2 CH_4(g) + O_2(g) \rightarrow {}^1/_2 CO_2(g) + H_2O(l) \tag{1.12}$$

then:

$$\Delta\xi = \frac{\Delta n_{CH_4}}{v_{CH_4}} = (-1)/(-{}^1/_2) = 2\,\text{mol} \tag{1.13}$$

and:

$$\Delta_m H = \frac{\Delta H}{\Delta\xi} = \frac{\Delta H}{(2)} = {}^1/_2 \Delta H \tag{1.14}$$

i.e. $\Delta_m H$ for reaction (1.12) corresponds to *half* $\Delta_m H$ for the reaction (1.3).

From the above it can be seen that a chemical equation gives a connection between $\Delta\xi$ and the various Δn.

These conclusions are used in application of Hess's Law (Frame 11, section 11.8).

The same principles above apply: to a *physical process* when represented as a chemical equation, for example:

$$Br_2(l) \rightarrow Br_2(g); \quad 298\,K, 100\,kPa \tag{1.15}$$

and to *any extensive function of state* (e.g. ΔU, ΔH, ΔS, ΔG etc.).

1.6 Types of Thermodynamic Function: Path Dependent Function, *q* and *w*

Path dependent changes result when *heat or work* are involved. Suppose we have a gas having a volume V_i which we heat up from T_i to T_f and then expand it (at a fixed temperature T_f) from the intial volume V_i to a volume, V_f. The heat supplied to the gas, q_1 and the work done, w_1, by the gas in expanding against external pressure *will be different* from the case where the gas is first expanded at fixed T_i from a volume V_i to V_f, doing work of expansion, w_2 and is then heated (q_2) from T_i to T_f ending up in the *same* final state (V_f, T_f) (Figure 1.1). It is easy to see that q_1 and q_2 are different from one another (i.e. they depend on the *precise* path followed). In the first case one is heating *a volume*, V_i, *of gas* whilst in the second case one is heating *a (larger) volume*, V_f *of gas*, both from T_i to T_f, and heat required (an extensive property) must be such that $q_2 > q_1$. Similarly for the work of expansion: w_1 expands the gas at the higher temperature T_f, and hence $w_2 < w_1$.

We shall discuss adoption of a convention for the *sign* for work of expansion – (Frames 7, 9, 14 and 15) and use it when we discuss in more detail the gas expansion processes (Frame 9). Also (FIRST LAW OF THERMODYNAMICS – see Frames 2, 8) the internal energy change, ΔU for the *overall process* in Figure 1.1 (i.e. gas at V_i and $T_i \rightarrow$ gas at V_f and T_f) (being a state function) is identical for both paths between the SAME initial and final states (and so is *route independent*).

Here *energy is neither created nor destroyed but merely converted from one form to another (i.e. heat and work, w → internal energy)*. Hence for the *specific* processes in Figure 1.1:

$$q_1 + w_1 = q_2 + w_2 = \Delta U_1 = \Delta U_2 = \Delta U$$

$$\text{although: } q_1 \neq q_2 \text{ and } w_1 \neq w_2 \qquad (1.16)$$

The First Law (equation 1.16) is subject to the constraint that we are not allowed to change the internal energy, ΔU, by adding or removing material. Equation (1.16) applies to a closed (but not necessarily unreactive) system.

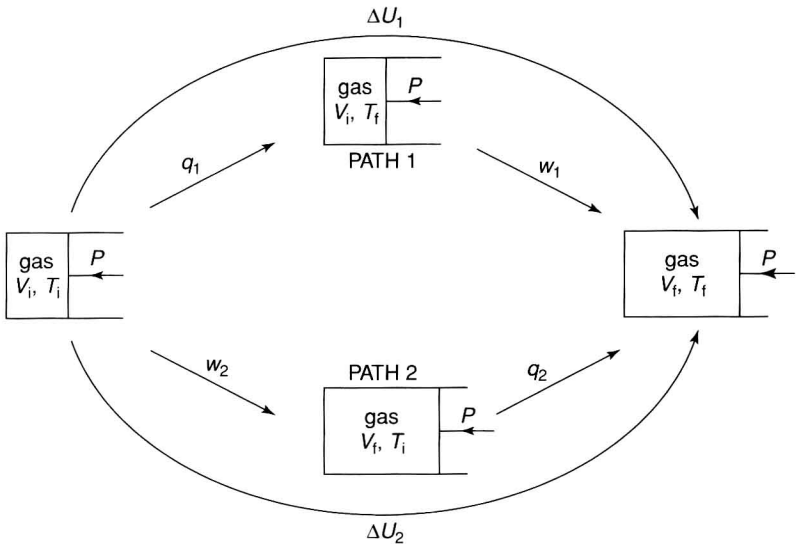


Figure 1.1 Comparison of path dependent functions (q and w) and path independent change (ΔU) during the expansion of a gas from (V_i, T_i) to (V_f, T_f) via two different states (V_f, T_i) (path 1) and (V_f, T_i) (path 2). V and T represent the volume and temperature of the gas. q and w represent the heat absorbed by the gas and the work done by the gas on the surroundings in expanding against the external pressure, P. w_1 and w_2 are both negative (using the convention discussed in Frame 7) since work of expansion is expended by the gas and lost from the (gas) system.

1.7 State Functions, *X*

Properties that are *path independent* depend only on the conditions at the start and at the end stages of the change are referred to as *state functions.*

These are often denoted by *capitalised* (upper case) symbols (examples are:

Gibbs energy, G (Frames 13 and 18); Enthalpy, H (Frames 13, 18 and 19); Entropy, S (Frames 11, 13, 15 and 19); Internal Energy, U (Frames 1, 8 and 10); Volume, V; Pressure, P; Temperature, T ... etc.);

for a state function X, ΔX depends *only* on the *difference between* the *final value*, X_f *and* the *initial value* of the property, X_i for the process:

Since $\int_{X_i}^{X_f} dX$, the integral of the change in $X(= dX)$ can be written (Frame 2) as $[X_f - X_i]$ then ΔX can be equated to an integral:

$$\Delta X = [X_f - X_i] = \int_{X_i}^{X_f} dX \qquad (1.17)$$

ΔX is then the same *whatever* route or path is selected to achieve the change and hence is path independent.

Expanding equation (1.16), in more detail:

$$\Delta U_1 = q_1 + w_1 = q_2 + w_2 = \Delta U_2 = \Delta U = [U_f - U_i] = \int_{U_i}^{U_f} dU \qquad (1.18)$$

In Frame 9 we consider the expansion of an ideal gas along an isotherm (or constant temperature curve for which $dT = 0$) from (P_i, V_i) to (P_f, V_f). Whilst the state functions P and V show *identical* changes in the two expansion processes considered ($dP = P_f - P_i$); $dV = (V_f - V_i)$ the work done in the two cases is entirely different. Two routes (paths) are considered:

expansion proceeds *infinitely slowly* (= *reversibly*), the external pressure never more than dP(i.e. a very small increment) less than the internal gas pressure at any point in time. The work performed by the gas is the maximum possible $w = w_{max} = -nRT \ln(V_f/V_i)$ (sign convention explained in Frame 7);

expansion proceeds *irreversibly* and *not* as a succession of equilibrium positions. This expansion is akin to a situation where a gas confined inside a cylinder, under pressure, P_i at volume V_i is suddenly exposed to the external (constant) atmospheric pressure, $P_f = P_{atm}$. Gas flows out from the cylinder until the final volume is V_f and pressure is P_f. The work done (Frame 9), $w = -P_f \Delta V = -P_f(V_f - V_i)$ is only a fraction of that performed in the process above yet the initial and final states of the gas are identical. This illustrates, again, that w is a path dependent function.

2. Integration in Thermodynamics

Some of the examples which are related to thermodynamics provided later in this Frame are meant to provide a first exposure to these thermodynamic functions. Such functions will be explained later in greater detail. The intention in introducing them so early is to show how the integration process impinges on the derivation of a number of key equations. The reader should endeavour to follow the logic used although he/she may not appreciate fully, until later, the underlying thermodynamic context.

2.1 Standard Integrals: Integration of Sums of Functions

Four common integrals encountered in thermodynamics (and their results) are shown below:

$$\int_{x_i}^{x_f} \mathrm{d}x = [x]_{x_i}^{x_f} = [x_f - x_i] \tag{2.1}$$

$$\int_{x_i}^{x_f} x.\mathrm{d}x = \left[\frac{x^2}{2}\right]_{x_i}^{x_f} = {}^1\!/_2[x_f^2 - x_i^2] \tag{2.2}$$

$$\int_{x_i}^{x_f} x^n \mathrm{d}x = \left[\frac{x^{n+1}}{(n+1)}\right]_{x_i}^{x_f} = \frac{\left[x_f^{n+1} - x_i^{n+1}\right]}{(n+1)} \qquad (n \neq -1) \tag{2.3}$$

$$\int_{x_i}^{x_f} \left(\frac{1}{x}\right) \mathrm{d}x = [\ln x]_{x_i}^{x_f} = [\ln x_f - \ln x_i] = \ln\left(\frac{x_f}{x_i}\right) \tag{2.4}$$

The integrals shown above are called:

- *Definite integrals* – because they have limits imposed. Thus for example:

$$\mathrm{I}_{\text{definite}} = \int_1^4 x.\mathrm{d}x = \left[\frac{x^2}{2}\right]_1^4 = {}^1\!/_2[(4)^2 - (1)^2] = \frac{15}{2} \tag{2.5}$$

  as opposed to:
- *Indefinite integrals* – which have no limits specified. On integration of indefinite integrals a constant c has to be included. Thus for example:

$$\mathrm{I}_{\text{indefinite}} = \int x.\mathrm{d}x = \frac{x^2}{2} + \mathrm{c} \tag{2.6}$$

now:

$$\mathrm{I}_{\text{indefinite}} \text{ (when } x = 4) = (8 + \mathrm{c}) \tag{2.7}$$

and:

$$\mathrm{I}_{\text{indefinite}} \text{ (when } x = 1) = ({}^1\!/_2 + \mathrm{c}) \tag{2.8}$$

$$\mathrm{I}_{\text{definite}} \text{ (2.5)} = [\mathrm{I}_{\text{indefinite}} \text{ (when } x = 4) - \mathrm{I}_{\text{indefinite}} \text{ (when } x = 1)] = [(8 + \mathrm{c}) - ({}^1\!/_2 + \mathrm{c})] = 15/2 \tag{2.9}$$

where we see that the constant, c cancels out when we evaluate the integral as in equation (2.9).

The integral of the sum of two or more functions can be written as the sum of two or more separate integrals, thus:

$$\int [f(x) + g(x)]\mathrm{d}x = \int f(x).\mathrm{d}x + \int g(x).\mathrm{d}x \tag{2.10}$$

(for notation see Frame 3, section 3.1).

Constants (= c) can be taken outside the integral sign as mere multiples and are then unaffected by the subsequent integration taking place, thus:

$$\int \mathrm{c}.f(x).\mathrm{d}x = \mathrm{c} \int f(x).\mathrm{d}x \tag{2.11}$$

2.2 Area Underneath a Curve can be Obtained by Integration

Figure 2.1 displays the function (line): $y = 3x$, underneath which function, (i.e. between the limits $x = 0$ (origin) and $x = 4$) lies the shaded triangle. The base of the triangle, $b = 4$ units. The height, h, of this triangle is 12 units. The area of a triangle is given by ${}^1\!/_2$ (*base*) (*perpendicular height*) $= {}^1\!/_2 bh = 24$ units^2. This corresponds to the area between the line (curve) $y = 3x$ and the abscissa ($y = 0$), otherwise known as the x-axis. This area, A, can be expressed as an integral:

$$A = \int_0^4 y\mathrm{d}x = \int_0^4 3x.\mathrm{d}x = 3\int_0^4 x.\mathrm{d}x = 3[{}^1\!/_2 x^2]_0^4 = 3[{}^1\!/_2(16) - 0] = {}^1\!/_2(48) = 24 \text{ units}^2 \tag{2.12}$$

此为试读,需要完整PDF请访问: www.ertongbook.com