

Physico-Chemical Calculations in Science and Industry

H. Fromherz



PHYSICO-CHEMICAL CALCULATIONS IN SCIENCE AND INDUSTRY

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PREFACE TO THE ENGLISH EDITION

IN THIS book, an attempt has been made to add a touch of realism to the theorems and formulae of physical chemistry by selecting, working out and explaining a variety of typical problems taken from the realms of science and industry.

It is hoped that the material will help students of chemistry, physics and related disciplines towards a better understanding of physical chemistry and its methods of calculation. As a practical reference book, the Exercises provide many examples of the almost limitless applications of physical chemistry to industrial problems. Ability to deal with these problems should prove useful in saving time and money and may even help in reducing loss of human life.

During his many years of experience as university teacher and industrial research chemist, and in his manifold dealings with students, discussion with professional colleagues and the tendering of advice, the author has had numerous opportunities to recognize just where the difficulties of appreciation and application of physical chemistry appear to lie.

Bearing in mind the purpose of the book, the order of the Exercises is such that, at any stage, it will generally be unnecessary to refer to later chapters. Moreover (with very few exceptions and at the risk of repetition), each problem is discussed so thoroughly that there is no need first to study other sections in order to understand it.

Corresponding to the diversity of practical problems, the Exercises will be found to vary between easy and more difficult, short and long. Rigid uniformity of expressions, terms and units of measurement, as used in textbooks, have been deliberately avoided. On the other hand, a uniform notation of formulae consistent with international usage has been adopted in order not to conflict with related sciences. This is especially so in the case of thermodynamic formulae.

For the sake of easy reference, the various Exercises are marked as follows:

Exercises particularly suitable for the practice of physical chemistry and its methods of calculation in connection with lecture demonstrations and problems are marked with an asterisk (*).

Difficult exercises which presuppose a certain command of the precepts of physical chemistry are unmarked.

Two bold asterisks are used to indicate those exercises which constantly recur in the typical calculations of physical chemistry and physico-chemical technology and which are presented in such a form as to be suitable for reference purposes.

This classification is to some extent arbitrary. Naturally, there are numerous examples which fall into more than one category.

The scientific requirements of the book have been related to those of the appropriate textbooks of physical chemistry from which derivations and explanations of

fundamental formulae have been taken and introduced at the beginning of each Chapter. It was not possible to include a list of books consulted in assembling the Exercises, but it must be mentioned that the following works were particularly helpful to the author in providing numerous references:

- D'ANS, J. and LAX, E., *Taschenbuch für Chemiker und Physiker*
 BLADERGROEN, W., *Physikalische Chemie in Medizin und Biologie*
 BONHOEFFER, K. F. and HARTECK, P., *Grundlagen der Photochemie*
 EGGERT, J. (with HOCK, L. and SCHWAB, G.-M.), *Lehrbuch der physikalischen Chemie*
 EMELÉUS, H. J. and ANDERSON, J. S., *Modern Aspects of Inorganic Chemistry*
 EUCKEN, A. and JAKOB, M., *Der Chemieingenieur*
 EUCKEN, A., *Lehrbuch der chemischen Physik*
 EUCKEN, A. and WICKE, E., *Grundriß der physikalischen Chemie*
 FAJANS, K. and WÜST, J., *Physikalisch-chemisches Praktikum*
 FETTKNECHT, W., *Allgemeine und physikalische Chemie*
 FIESER, L. F. and FIESER, M., *Organic Chemistry*
 FINKELNBURG, W., *Einführung in die Atomphysik*
 FROMHERZ, H. and KING, A., *German-English Chemical Terminology*
 GATTERMANN, L. and WIELAND, H., *Die Praxis des organischen Chemikers*
 GLASSTONE, S., *The Elements of Physical Chemistry*
 GLASSTONE, S., *Thermodynamics for Chemists*
 HERZFELD, K. F., *Kinetische Theorie der Wärme*
 HILDEBRAND, J. H., *Solubility of Non-electrolytes*
 HINSHELWOOD, C. N., *The Kinetics of Chemical Change in Gaseous Systems*
 HOFMANN, K. A., *Lehrbuch der anorganischen Chemie*
 HOLLEMAN, A. F. and WIBERG, E., *Lehrbuch der anorganischen Chemie*
 HÜCKEL, W., *Theoretische Grundlagen der organischen Chemie*
 JOST, W., *Explosions- und Verbrennungsvorgänge in Gasen*
 JUSTI, E., *Spezifische Wärme, Enthalpie, Entropie, Dissoziation technischer Gase*
 KARRER, P., *Lehrbuch der organischen Chemie*
 KNOX, J., *Physico-chemical Calculations*
 KOHLRAUSCH, F., *Praktische Physik*
 KORTÜM, G., *Einführung in die chemische Thermodynamik*
 KORTÜM, G. and BUCHHOLZ-MEISENHEIMER, H., *Theorie der Destillation und Extraktion von Flüssigkeiten*
 KORTÜM, G., *Lehrbuch der Elektrochemie*
 KUHN, W., *Physikalische Chemie*
 LEWIS, G. and RANDALL, M., *Thermodynamics*
 MICHAELIS, L., *Wasserstoffionenkonzentrationen*
 MICHAELIS, L., *Oxydations- und Reduktionspotentiale*
 MOELWYN-HUGHES, E. A., *The Kinetics of Reactions in Solution*
 PAULING, L., *General Chemistry*
 REMY, H., *Lehrbuch der anorganischen Chemie*
 SCHUMACHER, H. J., *Chemische Gasreaktionen*
 SCHWAB, G.-M., *Handbuch der Katalyse*
 SCHWAB, G.-M., *Katalyse vom Standpunkt der chemischen Kinetik*

SCHWABE, K., *Fortschritte der pH-Meßtechnik*

SCHWABE, K., *Polarographie und chemische Konstitution organischer Verbindungen*

SKRABAL, A., *Homogenkinetik*

ULICH, H. and JOST, W., *Kurzes Lehrbuch der physikalischen Chemie*

The number and choice of the calculations dealt with in individual chapters have not been determined by the extent and completeness of relevant chapters in textbooks where didactic requirements must be borne in mind; rather have they been framed according to type and variety of applications in science and industry, with the intention of giving a picture of those points having importance and usefulness in practice.

Physical calculations are often required in the realms of atomic and molecular structures, spectroscopy and the statistical theory of matter, but experience shows that the difficulties lie more in understanding trains of thought and in deductions than in making purely practical application. The latter is mostly a simple matter of inserting numerical values in established formulae; if not, the problems range beyond the limits of normal routine calculations and belong to the field of physical research. Calculation of the efficiency and regulation of distillation columns on the basis of the mixture equilibrium curve has also not been included as an example of chemical engineering.

On the other hand, different questions relating to chemico-physical practice are discussed in the way in which they would be encountered by the industrial chemist. Thus it will be shown that by using semi-empirical laws and sufficient approximation, solutions may often be found the apparent basic value of which is comparatively limited. However, on the whole, these solutions satisfactorily fulfil their purpose, i. e. the speedy and adequate answering of a question.

My thanks are due to Mr. G. Kinner who undertook the task of translating the second German edition of this book, and to the staff of Butterworths for their friendly care in its production.

Finally, professional colleagues are requested to support the author in his endeavour to place in the hands of students and colleagues a book on the applicational possibilities and calculation procedures of physical chemistry, which is as versatile and generally useful as possible – by advising him of their experiences, giving examples from their own sphere of activities and by bringing to his attention mistakes and suggesting improvements.

Schwyz, January 1964

H. F.

PREFACE TO THE SECOND EDITION

HEAVY demand has necessitated an early new edition of this book. Due account has been taken in the second edition of suggestions and critical remarks made by colleagues both in correspondence and in reviews. In particular, the dimensional notation has been made more precise and in the Chapter dealing with electromotive force a number of terms and formulae has been taken from the latest textbooks and publications in this field. I am indebted to Dr. E. Doehlemann, Trostberg (Obb.), for material regarding a new problem (No. 140.1) in electrometric titration. Four new Exercises on radioactivity have also been included; Nos. 207, 208, 209 on indicator analysis and No. 210 on protection against radiation. Thanks are due to Dr. E. Proksch, Vienna, for the material for Nos. 207, 208 and 209. The important eigenvalue method for the solution of differential equations, as well as the method for the variation of constants, given in problem No. 184 on the time dependence of a complex series of reactions, has been treated in a detailed and comparative manner.

Above all, I am grateful to Prof. Dr. G. Emschwiller, Paris, Prof. Dr. K. Huber, Berne, Prof. Dr. E. Lange, Erlangen, Prof. Dr. K. Peters, Vienna, and Prof. Dr. K. Schwabe, Dresden, for valuable suggestions and constructive criticism.

Schwyz, Autumn 1959

PROF. DR. HANS FROMHERZ

LIST OF SYMBOLS

A	work (fed into a system, or done on a system) activation energy surface area actual air consumption
A_0	theoretical air consumption
a	adsorbate, in millimoles per gramme adsorbent activity initial concentration constant in van der Waals equation of state quantity
α	degree of dissociation mole volume or surface fraction steric factor (probability factor) constant in Brønsted equation
α_{Bu}	Bunsen absorption coefficient
α_{Os}	Oswald absorption coefficient
B	constant in Freundlich adsorption isotherm second virial coefficient
b	constant in van der Waals equation of state constant in Langmuir adsorption isotherm
β	degree of dissociation constant for regular mixtures
C	Sutherland constant distribution coefficient conductivity
C, C^*	number of components (in phase rule)
C_p	heat capacity of a system at constant pressure
C_v	heat capacity of a system at constant volume
c	concentration, litre molarity (molarity) speed of light constant in Brunauer-Emmett-Teller adsorption isotherm
c_2	Planck's second constant ($= hc/k$)
c_p	specific heat per molecule (molar heat) at constant pressure
c_v	specific heat per molecule (molar heat) at constant volume
D	torsional moment diffusion coefficient
d	layer thickness
δ	boundary layer thickness
E	electromotive force (e.m.f.) voltage, terminal voltage, cell voltage
E_h	reference e.m.f. against the standard hydrogen electrode
E_{oh}	standard reference e.m.f. against the hydrogen electrode under standard conditions
E_0	standard e.m.f.
E_b	ebullioscopic constant
E_f	cryoscopic constant
e	electronic charge ($= F/N_A$)
ϵ	dielectric constant
η	internal friction coefficient yield (chemical efficiency)

List of symbols

F	force melting point 1 faraday (Faraday constant) degrees of freedom (in phase rule)
f	activity coefficient
f_{\pm}	mean activity coefficient
f_{λ}	conductivity coefficient
f_o	osmotic coefficient
Φ	molar enzyme concentration in Michaelis-Menten equation light intensity, radiation intensity
φ	angle specific volume concentration of enzyme-substrate complex in Michaelis-Menten equation lattice energy quantum yield efficiency
G	mass, especially to indicate kilogramme molarity, m free enthalpy (thermodynamic potential); Gibbs free energy
g	acceleration due to gravity
g, g'	constants in the Brønsted equation
Γ	ionic concentration
γ	degree of hydrolysis constant for regular mixtures specific gravity
H	enthalpy (heat content)
H, H'	frequency factor (action constant)
ΔH^E	heat of formation
H_G, H_N	gross and net calorific value
h, H	height, fall
h	Planck's constant
I	electric current strength total radiation/sec unit matrix
J, J^*	ionic strength
i	van't Hoff coefficient
K	transformation matrix number of independent equilibrium constants (in phase rule)
K, K_c, K_p, K_x	law of mass action constants proportionality factor
K_p	boiling point
K_{p100}	boiling point at 100 torr
K_s	solubility product
k	constant in Henry's law bulk modulus reaction rate constant Boltzmann constant ($= R/N_A$)
k_A	Smythe factor
k_{H_2O}	ionic product of water
κ	ratio of the specific heats, c_p/c_v specific conductivity
L	tube or cell length
L_f	enthalpy of fusion
L_s	enthalpy of sublimation
L_t	enthalpy of transition
L_v	enthalpy of vaporization

List of symbols

l	mean free path
dI^*	final heat of solution
l_f	molar enthalpy of fusion
l_s	molar enthalpy of sublimation
l_t	molar enthalpy of transition
l_v	molar enthalpy of vaporization
$\Lambda_{c(mol)}$	molar conductivity
$\Lambda_{c(eq)}$	equivalent conductivity
$\Lambda_{K(eq)}, \Lambda_{A(eq)}$	ion equivalent conductivity
λ	wavelength
	excess air coefficient
	molar reaction variable
	radioactive decay constant
	eigenvalue
λ	first heat of solution
λ_f	enthalpy of fusion per gramme
λ_v	enthalpy of vaporization per gramme
M	molecular weight, atomic weight in the meaning of (i) molar mass (g/mole), (ii) molecular weight (ratio)
\bar{M}	mean or apparent molecular weight of a mixture
M_r	reduced mass
m	mass
	concentration (mole/kg solvent), kilogramme molarity (molality)
m, μ	extinction modulus (absorption coefficient, attenuation coefficient)
Nm^3	cubic metres at s.t.p. (1 atm, 0°C)
N	number of particles
	output, power
\dot{N}	particle velocity ($= dN/dt$)
1N	number of particles per cm^3
1N_i	number of particles of substance X_i per cm^3 of mixture
N_A	number of molecules in one mole (Avogadro constant)
n	quantity of moles, quantity of equivalents
	adsorption isotherm constant
n_e	electrochemical valency of an electrolyte; cell reaction charge number or number of faradays transported per mole-formula-weight change
n_A, n_K	transport numbers
$\{n_q\}$	number of mol. quanta
\dot{n}_q	number of mol. quanta per unit time and per unit volume
ν	number of fragments from a dissociating molecule
ν_i	stoichiometric mole number
	frequency ($= c/\lambda$)
ν	wave number ($= 1/\lambda$)
P	osmotic pressure
	pressure (only used in certain cases, especially for distinction from pH)
	number of phases (in phase rule)
p, p^*	pressure
	fugacity
	statistical constant in Brønsted equation
pH	negative logarithm of hydrogen ion activity
p_i	partial pressure of substance X_i
p_{0i}	vapour pressure of pure substance X_i (saturation pressure)
p_k	critical pressure
π	Ludolph's number

Q	heat supplied to a system quantity of electricity, in coulombs
q	cross-sectional area statistical factor in Brønsted equation
Ω_p	heat of reaction at constant pressure ($= -\Delta H$)
Ω_v	heat of reaction at constant volume ($= -\Delta U$)
R	electrical resistance gas constant ($= N_A k$)
r	mixture ratio radius
rH	negative logarithm of hydrogen pressure
ρ	density
S	entropy specific activity of a radioactive substance
$[S]$	substrate concentration
S_{0298}	standard entropy
Σ	summation symbol
σ	molecular diameter specific resistance
σ_{12}	mean molecular diameter ($= r_1 + r_2$)
T	absolute temperature, in degrees Kelvin half-life period
T_k	critical temperature
t	separation factor time
t_r	residence time
τ	mean life period
θ	temperature, in degrees Centigrade
U	(internal) energy
u_A, u_K	absolute migration velocity (per V/cm), ionic mobility
V	volume
\dot{V}	volumetric rate ($= dV/dt$)
v	molar volume reaction velocity ($= dz/dt$)
v_k	critical volume per mole
W	weight
w	speed; molecular speed
\bar{w}	mean molecular speed
X	frictional force; force
x	eigenvector
x	coordinate value quantity (of adsorbate) mole fraction magnitude of an unknown
100 x	mole per cent
ξ	weight or mass fraction
100 ξ	per cent by weight
Y	Einstein constant for the mass-energy relation ($= c^2$)
y	magnitude of an unknown
Z	collision number constant in wave number-energy relation ($= N_A h c$) pore number
z, z_+, z_-	ionic charge; ion valency
z_s	number of adsorption centres

CONTENTS

	Page
Preface to the English Edition	IX
Preface to the Second Edition	XIII
List of Symbols	XV
Introductory Remarks on Symbols and Equations	1
1 Ideal Gases	4
2 Gas Dissociation	19
3 Real Gases and Liquids	22
4 Kinetic Theory of Gases. Effusion, Flow, Diffusion	28
5 Concentration of Mixtures and Solutions	40
6 Vapour Pressure of Liquid Mixtures and Solutions. Azeotropy. Miscibility Gaps	47
7 Determination of Molecular Weight in Solutions	74
8 Temperature Dependence of Vapour Pressure. Determination of Heats of Vaporization, Sublimation and Fusion	81
9 Thermochemistry: Heat of Reaction. Temperature Dependence. Specific Heat	99
10 Chemical Equilibrium at Constant Temperature. Law of Mass Action. Distribution Law. Gas Solubility	121
11 Temperature Dependence of Chemical Equilibria. Absolute Calculation of Chemical Equilibrium	167
12 Electrochemistry: Ionic Theory and Ionic Equilibria	189
13 Electromotive Force: Galvanic Cells. Redox Electrodes. Decomposition Voltage, Polarization, Polarography. Batteries, Overvoltage. Diffusion Potential, Membrane Potential	228
14 Reaction Kinetics and Catalysis. Chain Reactions. Photochemistry. Radioactivity. Adsorption	260
Tables: Constants and Conversion Factors	339
Conversion of Energy	340
Periodic System of Elements	342
Subject Index	343

INTRODUCTORY REMARKS ON SYMBOLS AND EQUATIONS

IN THIS book it has been assumed that the indication of dimensions should promote clarity in presentation, but should not become an end in itself.

In general, the following principles are adopted:

(1) As a rule the symbols signify physical quantities, i.e. the products of a numerical value and a dimension; not numerical values only.

Example—For the unit G one may put

$$G = 5.3 \text{ g} = 5.3 \times 10^{-3} \text{ kg} \quad \text{but not } 5.3 \quad \text{or } 5.3 \times 10^{-3}$$

For the pressure, p , one may have

$$p = 10 \text{ atm} = 7600 \text{ torr} = 10.33 \text{ kg cm}^{-2}, \text{ but not } 10 \text{ or } 7600.$$

As a rule, therefore, relations between symbols represent equations between quantities.

(2) If, in certain cases, for example for logarithms, only the coefficient $\{ \}$ is used, without the selected unit of measurement (dimension), a special note is made, should clarity require it.

Example: $p = 10 \text{ atm} = 7600 \text{ torr}$

$$\log p/\text{atm} = 1.0 \quad \text{or} \quad \log p/\text{torr} = 3.881$$

or just

$$T = 1000 \text{ }^\circ\text{K} \quad \{T\} = 1000 \quad \log \{T\} = 3$$

It is usually unnecessary to write $\log T/\text{deg.} = 3$, since, in scientific works, T is always measured in the same units.

(3) For the sake of clarity:

(a) in equations in which a combination of symbols and numerical quantities occurs, the units of measurement of the numerical quantities will, as a rule, be omitted, e.g. $T = T_0 + \theta = 273 + \theta$, and not $T = 273 \text{ deg.} + \theta$ or $T = (273 + \{\theta\}) \text{ deg.}$

(b) as a rule, in making numerical calculations, only numerical values will be given in the intermediate steps, the unit of measurement being quoted only in the final result, provided that the dimensions are not changed during the calculation and a dimensional check is not required, e.g. $p = 677 + 8 = 685 \text{ torr}$, and not $p = (677 + 8) \text{ torr} = 685 \text{ torr}$

$$G = \frac{MpV}{RT} = \frac{32 \times 150 \times 40}{0.082 \times 288} = 8130 \text{ g} = 8.13 \text{ kg}$$

not, in general

$$G = \frac{32 \text{ g mole}^{-1} \times 150 \text{ atm} \times 401.}{0.082 \frac{\text{l. atm}}{\text{deg. mole}} \times 288 \text{ deg.}} = \frac{32 \times 150 \times 40}{0.082 \times 288} \frac{\text{g mole}^{-1} \text{ atm l.}}{\text{l. atm deg.}^{-1} \text{ mole}^{-1} \text{ deg.}} = 8130 \text{ g}$$

(4) The symbol n represents the quantity of a substance in moles (gram mols), that is the molar quantity with the unit of measurement [mole], e.g. $n = 5.2$ moles; the symbol $\{n\}$ represents the dimensionless number of moles, e.g. $\{n\} = 5.2$, i.e. $n = \{n\}$ moles.

(5) In physico-chemical calculations it is preferable to use related quantities. Thus, in general, quantities will relate to 1 mole or 1 equivalent of substance.

Examples

Gas constant $R = 1.9865$ cal/(deg. mole)

and not

molar gas constant $R = 1.9865$ cal/deg.

Avogadro (Loschmidt) constant $N_A = 6.0236 \times 10^{23}$ mole⁻¹

and not

Avogadro (Loschmidt) number $N_A = 6.0236 \times 10^{23}$

Faraday constant F (1 faraday) = 96,495 coulomb/equiv.

and not

Faraday-equivalent $F = 96,495$ coulomb.

It is evident that what appears to be an unnecessary duplication of expressions is expedient in order to give a clear presentation; e.g. the *molar volume* of water is $v_{H_2O} = 18$ cm³/mole, is used instead of the *volume* of water is $v_{H_2O} = 18$ cm³/mole; or the *molar heat* of water is $\bar{c}_p = 18.02$ cal/deg. mole instead of the *heat capacity* of water is $\bar{c}_p = 18.02$ cal/deg. mole.

(6) A reaction equation will be written in the usual manner:



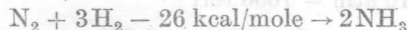
or



or



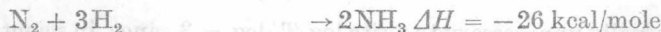
e.g.



or



or



It should indicate the conversion of molar quantities of the substances X_i . ΔH is the heat of reaction for a reaction in which the molar quantities n_i are converted, and therefore has the units [kcal/mole] or [joule/mole], as has also the external work, $p\Delta V$, appearing during the reaction. The molar quantity n_i (unit [mole]) is normally (see p. 101) broken down to $n_i = \nu_i \lambda$ or $dn_i = \nu_i d\lambda$, where ν_i is the stoichiometric mole number of the substance X_i (dimensionless) and λ is the molar 'reaction variable' (degree of advancement) (unit [mole]) of the relevant reaction. The name introduced above has been retained although, in accordance with the definitions in this book, λ represents a quantity of substance with the unit [mole]: when the reaction proceeds according to formula, λ is equal to 1 mole.

Example—5 moles N_2 and 15 moles H_2 are converted to 10 moles NH_3 . As a result, 130 kcal are liberated at 500 °C. The stoichiometric mole numbers are $\nu_i = 1, 3$ and 2; the reaction variable is

$$\lambda = \frac{5 \text{ moles}}{1} = \frac{15 \text{ moles}}{3} = \frac{10 \text{ moles}}{2} = 5 \text{ moles}$$

The heat of reaction, per formula conversion, is

$$\Delta H = \frac{-130 \text{ kcal}}{5 \text{ moles}} = -26 \text{ kcal/mole}$$

(7) As is customary in textbooks of chemistry and physics, the symbol M has been taken to indicate molecular weight. However, in equations it may have a dual meaning — but the same numerical value — as follows:

(a) Molar weight in grammes (mass of a mole) with the dimensions (g/mole), e.g. $M_{\text{C}_6\text{H}_6} = 78.1 \text{ g/mole}$ means that the molar weight of benzene is 78.1 g.

(b) 'Molecular weight' which, as is well known, is neither a weight nor a mass but a non-dimensional ratio and should, therefore, correctly be designated by $\{M\}$ ($M = \{M\}$ grammes), e.g. $M_{\text{C}_6\text{H}_6} = 78.1$, means that benzene has a molecular weight of 78.1.

Neither in designation nor in calculation is there any danger of confusion in establishing this point—even though international agreement of the concept may be desirable.

(8) In chemistry one is usually interested in the mass G of a substance, expressed in the units gramme (g) or kilogrammes (kg). The chemist's analytical balance serves to compare masses. In those cases where weight W is expressly used, gramme weight (g wt.) and kilogramme weight (kg wt.) are the terms used.

Example—The density of air is $\rho = 1.293 \times 10^{-3} \text{ g/cm}^3 = 1.293 \text{ g/l.}$, but the weight of air (specific gravity) is $\gamma = 1.293 \times 10^{-3} \text{ g wt./cm}^3 = 1.293 \text{ g wt./l.}$

The heat of reaction per mole is given by

$$\Delta H = -120 \text{ kcal} - (-78 \text{ kcal}) = -42 \text{ kcal/mole}$$

(7) As is customary in textbooks of chemistry and physics, the symbol M has been taken to indicate molecular weight. However, in equations it may have a dual meaning – but the same numerical value – as follows:

1

IDEAL GASES

If an ideal gas has the pressure p_1 and volume V_1 at the absolute temperature T_1 , and pressure p_2 and volume V_2 at absolute temperature T_2 , then

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} = \text{const} \quad \dots \quad (1)$$

T (degrees Kelvin, °K) = $T_0 + \theta = 273.16 + \theta$ (θ in degrees Centigrade, °C)

In general:

$$pV = nRT = \frac{G}{M} RT \quad \dots \quad (2)$$

the equation of state for ideal gases.

$$n = \text{molar quantity (mole)} = \frac{\text{mass } G(\text{g})}{\text{mol. wt. } M(\text{g/mole})} \quad \dots \quad (3)$$

(See p. 2, paras. 4 and 6.) R is the gas constant.

If $p_0 = 1 \text{ atm}$, $T_0 = 273.16^\circ \text{K}$ or 0°C (standard conditions), the volume of 1 mole of a gas (molar volume) is $v_0 = V_0/n = 22,415 \text{ cm}^3/\text{mole}^{-1} = 22.415 \text{ l. mole}^{-1}$.*

$$\begin{aligned} \text{Thus: } R &= \frac{p_0 V_0}{n T_0} = \frac{1 \times 22415}{1 \times 273.16} = 82.06 \text{ cm}^3 \text{ atm/deg. mole} \\ &= 0.80206 \text{ l. atm./deg. mole} = 1.9865 \text{ cal/deg. mole} \end{aligned} \quad \dots \quad (4)$$

The density of an ideal gas is ρ_0

$$= \frac{\text{Mol. wt. } M}{\text{Molar volume } v_0} = \frac{\{M\}}{22,415} \frac{\text{g}}{\text{Ncm}^3} = \frac{\{M\}}{22,415} \frac{\text{g}}{\text{l.}} \quad (\text{see p. 3, para. 7}) \quad \dots \quad (5)$$

For an ideal gas mixture, the total pressure, p , is equal to the sum of the partial pressures p_i of the components X_i , thus

$$p = p_1 + p_2 + \dots = \sum p_i \quad \text{Dalton's law} \quad \dots \quad (6)$$

If all mixture components X_i have the same pressure p and if p remains constant, then the volume of the mixture is equal to the sum of the individual volumes V_i , thus

$$V_m = V_1 + V_2 + \dots = \sum V_i \quad \dots \quad (7)$$

* Gas volume reduced to standard temperature and pressure (0°C , 760 torr) is measured in normal cubic metres, Nm^3 , or normal cubic centimetres, Ncm^3 . Gas pressure is measured either in physical atmospheres [atm], or in mm Hg = torr ($1 \text{ atm} = 760 \text{ torr} = 1033.23 \text{ g wt./cm}^2$) or in kg wt./cm^2 ; $1 \text{ kg wt./cm}^2 = 1000 \text{ g wt./cm}^2 = 735.559 \text{ torr}$.

In the c.g.s. system the unit of measurement for pressure is $\text{dyn/cm}^2 = \text{microbar}$. $1 \text{ atm} = 1.01325 \times 10^6 \text{ dyn/cm}^2 = 1013.25 \text{ millibars (mb)}$; $1 \text{ torr} = 1 \text{ mm Hg} = 1.33322 \times 10^3 \text{ dyn/cm}^2 = 1.33322 \text{ mb}$ (see also p. 3, para. 7 and p. 8).

The equation of state for an ideal gas mixture is therefore

$$\left. \begin{aligned} pV_m &= (n_1 + n_2)RT = \sum n_i RT = \sum \frac{G_i}{M_i} RT = \frac{G}{\bar{M}} RT \\ p_i V_m &= n_i RT = \frac{G_i}{M_i} RT \quad \text{or} \quad p_i = \frac{n_i}{V_m} RT = c_i RT \end{aligned} \right\} \dots (8)$$

[c_i = concentration in moles per unit volume, see also eqn. (58)]

In this equation G_i is the mass (g) and M_i the molar weight (g/mole) of the component X_i . G , the total mass of the gas mixture, is given by $G = G_1 + G_2 + \dots = \sum G_i$ and \bar{M} is the mean or apparent molar weight.

According to eqn. (8) the mean molar weight, \bar{M} , will be

$$\bar{M} = \frac{G}{\sum n_i} = \frac{G_1 + G_2 + \dots}{n_1 + n_2 + \dots} = \frac{n_1 M_1 + n_2 M_2 + \dots}{\sum n_i} = x_1 M_1 + x_2 M_2 + \dots = \sum x_i M_i \dots (9)$$

x_i = the mole fraction of component X_i

$$x_i = \frac{n_i}{\sum n_i} = \frac{G_i/M_i}{\sum G_i/M_i} = \frac{p_i}{p} \quad (\text{according to Avogadro}) \dots (10)$$

$$\left. \begin{aligned} \text{The mole per cent (mole \%)} &= \text{mole fraction} \times 100 = x_i \times 100 \\ &= \frac{G_i/M_i}{\sum G_i/M_i} \times 100 \\ &= \text{volume per cent (vol.\%)} \text{ for ideal gases} \end{aligned} \right\} \dots (11)$$

According to eqns. (10) and (11), the following may be used for conversion of weight per cent (wt. %) $100\xi_i$ (ξ_i = proportion by weight or mass) to mole per cent and vice versa:

$$\left. \begin{aligned} \text{mole per cent:} & \quad 100 x_i = \frac{100 \xi_i/M_i}{\sum \xi_i/M_i} \\ \text{wt. per cent:} & \quad 100 \xi_i = \frac{x_i M_i}{\sum x_i M_i} \quad 100 = 100 \frac{x_i M_i}{\bar{M}} \end{aligned} \right\} \dots (12)$$

For the mean molar weight, it follows from eqns. (9) and (12) that

$$\bar{M} = \frac{1}{\sum \xi_i/M_i} \dots (13)$$

and, from eqns. (12) and (13), for mole per cent:

$$100 x_i = 100 \xi_i \bar{M}/M_i \dots (14)$$

$$\text{or mole \%} = \text{wt. \%} \times \frac{\text{mean mol. wt.}}{\text{mol. wt.}}$$

*EXERCISE 1

Calculate, from the molecular weight, the density ρ_0 in g/l. for oxygen, nitrogen, carbon monoxide and nitric oxide [see eqn. (5)].