PHYSICAL CHEMISTRY THROUGH PROBLEMS

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Preface

A proper understanding of the principles of physical chemistry is required for a study of pure, industrial and biological sciences. It is the authors opinion that these principles can be learnt properly only through their applications to solving problems and that the existing texts do not prepare a student sufficient in the diverse applications of the fundamental principles of physical chemistry. This book has been written to fill this gap.

The topics in this book have been put in the time tested arrangement of first structure, then dynamics and lastly synthesis. The first two fall in the domain of the physical chemistry proper and last in that of organic and inorganic chemistry. The first four chapters are devoted to the understanding of the elementary quantum mechanics and atomic and molecular structure. The care has been taken to give problems which illuminate the principles of atomic and molecular structures. So that the students can grasp the more involved details that follow. Chapter five illustrates the physical methods used in establishing the structures and parameters of molecules. Chapter six, seven and eight give the preliminary ideas about the three states of matter, i.e. solids, liquids and gases. Chapter nine serves as a bridge between the results of microsystems and their applications to the macrosystems, i.e. statistical mechanics. This chapter illustrates the methods of calculating the properties of bulk system from those of microsystems. Chapters 10 to 17 deal with the principles of thermodynamics and electrochemistry applicable to ideal systems. These help in determining whether particular process, physical or chemical, is feasible or not. Chapter deals with quantities that measure the departure of real systems from ideal behaviour. The basic principles of chemical kinetics are dealt in Chapter 19. This helps in following the progress of a process.

Each section of a chapter starts with a short summary of the basic fundamentals to refresh the memory of the students and to place in perspective the results required for solving problems. This is followed by illustrations. At the end of each chapter there are number of un-solved problems, arranged in the order in which concepts have been introduced. The answers of these problems are given at the end. Care has been taken to provide all the data needed for a particular problem but a hand-book may be consulted wherever proper data has not been given.

The SI units have been used predominently, though some non-SI units like those for pressure etc. have been used along side. This is because a large amount of information is still available in non-SI units

and the students should be familiar with both the systems.

A large number of problems enclosed in this book have been tested on first and second year students of the B. Tech. programme and on the M Sc. students, studying at I.I.T. Kanpur. The data needed in these problems have been taken from International critical tables, hand book for physics and chemistry, journals and physical chemistry text books. The authors acknowledge their debt. We also express our thanks to Mr. R.D. Singh and Mr. Anil Kumar for typing the manuscript and to Mr. B.S. Panesar for the preparation of drawings. The authors also acknowledge the financial grant from the curriculum development group of quality improvement programme at Indian Institute of Technology, Kanpur. Finally we would like to express our sincere thanks to Mr. S.N. Mahey (late) whose constant encouragement has made possible to complete this work.

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SI Units

1.1 Introduction

In normal day-to-day life, although variety of units have been used but in scientific world mainly two systems of units are commonly used. One is F.P.S. (Foot, Pound and Second), originated in U.K. and other cgs. (Centimetre, Gram and Second) originated in France. As the definitions stand today, foot or cm is a distance between the two fixed marks on a specific kind of metal, pound is a weight of a certain mass of metal whereas a gm used to be (originally specified) as a mass of one cubic centimetre of water at 0°C. The kilogram was later specified as being the mass of a particular piece of metal.

For a common man units of measure do not matter much and he will prefer to use the same units which he is using for centuries. But in the scientific world, if there is no common language it is not easy to understand the discoveries or an achievement of scientists of different countries, since the knowledge of science does not remain in domain of one person or of one country. The other major disadvantage of the present system of units is that they are not in any way derivable from the scientific formulas or natural constants. So the need was felt to arrive at a common system of units. The meeting was held under the auspicious of Conference Generale des Poids et Messues (C.G.P.M.) and agreed to adopt common units of measurements known as Systeme Internationale d' Units or the International System of Units, the abbreviation of which is SI. Many countries have adopted this system of units.

According to SI, the unit for distance is 'metre (m)', defined as the length equal to 1 650 763.73 wavelengths in vacuum of the radiation corresponding to the transition between the levels $2p_{10}$ and $5d_5$ of the krypton-86 atom. The SI unit of area is the square metre (m^2). Land is often measured by the hectare (10000 m^2 or approximately 2.5 acres). The SI unit of volume is the cubic metre (m^3). Fluid volume is often measured by the litre (0.001 m^3 or dm^3).

The unit of time is second(s), defined as the duration of 9 192 631 770 periods of the radiation corresponding to the transition between two hyperfine levels of the ground state of the cesium-133 atom. The SI unit for frequency is the hertz (Hz) which equals one cycle per second.

The standard unit of mass, the kilogram (kg) is a cylinder of platinum-iridium alloy kept by the International Bureau of Weights and Measures

at Paris. It is important to note that unit of mass is not defined in terms of physical constants and is quite possible that the base unit of mass now known as kg will be renamed as giorgi, symbol G. The SI unit of force is newton (N), which is the force when applied for one second will give to a 1 kg mass a speed of 1 m per second. One newton equals nearly 0.2 lb of force. The SI unit for work and any kind of energy is the Joule (J), $1J = 1$ N.m. The SI unit for power of any kind is the Watt (W), $1\ W = 1\ Js^{-1}$.

The Kelvin or thermodynamic scale of temperature used in SI has its origin or zero point at absolute zero and has a fixed point at the triple point of water defined as 273.16 K. The triple point defined on Celsius scale is 0.01°C and on Fahrenheit scale as 32.02°F.

The basic unit of electric current is ampere (A), defined as the magnitude of the current that, when flowing through each of two long parallel wires separated by 1 m in free space, results in a force between the two wires (due to these magnetic fields) of 2×10^{-7} N for each metre of length. The SI unit of voltage is volt (V), which is defined $1\ V = 1\ WA^{-1}$. The SI unit of electrical resistance is the ohm (Ω) which is defined $1\ \Omega = 1\ VA^{-1}$.

It is good if the standard units are used every where. Certain units, e.g. minute, hour, day, litre, degree Celsius, degree (angle), minute (angle) etc. will be used simultaneously along with SI units for some times though these units have no place in scientific world. Of course units like scurie, electron volt, gauss, bar and barn will be used along with SI units but we hope that with time they will be phased out.

In the following pages the usages of SI units will be discussed by taking certain examples. It will be shown that SI units are much better and one does not need to remember the units of many quantities.

1.2 Special Notes on the Use of SI Units
1. Only the singular form of units is to be used, e.g. km and not kms.
2. Full stop at the end of abbreviations is to be omitted, e.g. km not km.
3. The decimal sign is to be a point or a comma on the line, e.g. 2.5 or 2, 5 not 2.5.
4. Digits should be grouped in threes about the decimal point in order to facilitate the reading of long numbers. Commas should not be used to space digits in numbers, e.g. 16 543 121.133 45 and not 16, 543, 121.133, 45.
5. The degree sign is to be omitted when the Kelvin scale is employed, e.g. 273 K and not 273°K.
6. The solidus is not to be encouraged, but where used, no more than one should be employed, e.g. J $kg^{-1}K^{-1}$ or J/kg K but not /Kg/K.

1.3 Basic Units
The basic units of the SI system are shown in Table 1.1.

TABLE 1.1 Base Units

Physical quantity	Unit	symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	kelvin	K
Luminous intensity of light	Candela	Cd
Plane angle	radian	rad
Solid angle	Steradian	srn

The mol has been recommended by the ISO (International Organisation for Standarisation) as a basic unit but this remains to be accepted by the CGPM.

1.4 Derived Units
Derived units with special names are given in Table 1.2.

1.5 Prefixes
It is recommended that prefixes to be used should differ from a unit in steps of 10^3 (Table 1.3).

Units to be eventually abandoned are listed in Table 1.4.

.6 Equations of Electromagnetism from cgs to SI
Table 1.5 gives the conversion factors for converting the equations representing the electromagnetic quantities from cgs to SI units, i.e. for each electromagnetic quantity expressed in cgs units, substitute the required value and rearrangement gives the desired quantities in SI units (see exercises 1.9 and 1.10).

TABLE 1.2   Symbols for Certain SI Derived Units

Physical quantity	Name of SI Unit	Symbol of SI Unit	Definition of SI Unit
Force	newton	N	$kg\ m\ s^{-2}$
Pressure*	pascal	Pa	$kg\ m^{-1}\ s^{-2}\ (=N\ m^{-2})$
Energy	joule	J	$kg\ m^2\ s^{-2}$
Power	watt	W	$kg\ m^2\ s^{-3}\ (J\ s^{-1})$
Electric charge	Coulomb	C	$A\ s$
Electric potential difference	volt	V	$kg\ m^2\ s^{-3}\ A^{-1}\ (=J\ A^{-1}\ s^{-1})$
Electric resistance	ohm	Ω	$kg\ m^2\ s^{-3}\ A^{-2}\ (=V\ A^{-1})$
Electric conductance*	Seimens	s	$kg^{-1}\ m^{-2}\ s^3A^2\ (=A\ V^{-1}=\Omega^{-1})$
Electric capacitance	farad	F	$A^2\ s^2\ kg^{-1}\ m^{-2}\ (=A\ s\ V^{-1})$
Magnetic flux	Weber	Wb	$kg\ m^2\ s^{-2}\ A^{-1}\ (=V\ s)$
Inductance	henry	H	$kg\ m^2\ s^{-2}\ A^{-2}\ (=V\ A^{-1}\ s)$
Magnetic flux density	Tesla	T	$kg\ s^{-2}\ A^{-1}\ (=V.s\ m^{-2})$
Luminous flux	lumen	Lm	$Cd\ sr$
Illumination	lux	lx	$Cd\ sr\ m^{-2}$
Frequency	hertz	Hz	s^{-1}

a.   recommended by CIPM.

TABLE 1.3   Prefixes for Fractions and Multiples of SI Units

Prefix	Symbol	Factor	Prefix	Symbol	Factor
tera	T	10^{12}	*centi	c	10^{-2}
giga	G	10^9	milli	m	10^{-3}
mega	M	10^6	micro	μ	10^{-6}
kilo	k	10^3	nano	n	10^{-9}
*hecto	h	10^2	pico	p	10^{-12}
*deca	da	10	femto	f	10^{-15}
*deci	d	10^{-1}	atto	a	10^{-18}

*An asterisk indicates that the use of these prefixes is limited to occasions where recommended prefixes are inconvenient.

TABLE 1.4

Physical quantity	Unit	SI equivalent
Length	*Angstrom (Å)	10^{-13} m
	*Inch (in)	0.0254 m
	mile	1.60934 km
	*nautical mile international	1.852 km
Area	*barn (b)	10^{-28} m²
	*square inch (in²)	645.16 mm²
Volume	cubic inch	1.63871×10^{-5} m³
Mass	*pound (lb)	0.453 592 37 kg
Force	*dyne (dyn)	10^{-5} N
	poundal	0.138 255 N
	pound force	4.448 22 N
Pressure	*atmosphere (atm)	101.325 kN.m⁻²
	*bar (bar)	105 N m⁻²
	torr (torr)	133.322 N.m⁻²
	p.s.i.	6 894.76 N m⁻²
Energy	*calorie international	4.1868 J
	calorie 15°C (cal$_{IT}$)	4.1855 J
	*calorie thermochemical (cal$_{th}$)	4 184 J
	B.t.u.	1055.06 J
	electron volt (eV)	1.6021×10^{-19} J
	*erg (erg)	10^{-7} J
Power	horse power	745.700 W
Radioactivity	*curie (Ci)	3.7×10^{10} s⁻¹
Exposure	roentgen (R)	2.5×10^{-4} C.kg⁻¹
Magnetic flux density	*gauss (G)	10^{-4} T
Kinematic viscosity	*stoke (St)	10^{-4}.m² s⁻¹
Dynamic viscosity	poise (P)	10^{-1} kg m⁻¹ s⁻¹

*An asterisk indicates that the conversions are exact.

TABLE 1.5   Expressions for Physical Quantities

Physical quantity	cgs symbol	SI symbol	Physical quantity	cgs symbol	SI symbol
Electric charge	Q	$(4\pi\varepsilon_0)^{-1/2}\,Q$	Resistivity	ρ	$4\pi\varepsilon_0\,\rho$
			Conductance	G	$G/4\pi\varepsilon_0$
Charge density	ρ	$(4\pi\varepsilon_0)^{-1/2}\,\rho$	Conductivity	K	$K/4\pi\varepsilon_0$
Surface charge density	σ	$(4\pi\varepsilon_0)^{1/2}\,\sigma$	Impedance	Z	$4\pi\varepsilon_0\,Z$
			Self-impedance	L	$4\pi\varepsilon_0\,L$
Electric dipole moment	p	$(4\pi\varepsilon_0)^{-1/2}\,p$	Capacitance	C	$C/4\pi\varepsilon_0$
			Speed of light	c	$(\mu_0\varepsilon_0)^{-1/2}$
Electric current	i	$(4\pi\varepsilon_0)^{-1/2}\,i$	Magnetic induction	B	$(4\pi\mu_0)^{1/2}\,B$
Electric current density	j	$(4\pi\varepsilon_0)^{-1/2}\,j$	Magnetic field strength	H	$(4\pi\mu_0)^{1/2}\,H$
Electric field strength	E	$(4\pi\varepsilon_0)^{1/2}\,E$	Magnetisation	M	$(\mu_0/4\pi)^{1/2}\,M$
Electric displacement	D	$(4\pi\varepsilon_0)^{1/2}\,D$	Electro-magnetic moment	m	$(\mu_0/4\pi)^{1/2}\,m$
Dielectric polarisation	P	$(4\pi\varepsilon_0)^{-1/2}\,P$	Relative permeability	μ	μ/μ_0
			Magnetic susceptibility	χ	$\chi/4\pi$
Electric potential	V	$(4\pi\varepsilon_0)^{1/2}\,V$			
Relative permittivity	ε	$\varepsilon/\varepsilon_0$			
(Dielectric constant)	D				
Electric polarisability	α	$\alpha/4\pi\varepsilon_0$			
Resistance	R	$4\pi\varepsilon_0\,R$			