PHYSICAL CHEMISTRY
Principles and Problems

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Preface

Physical chemistry forms an integral part of nearly all the branches of science, technology and engineering. Even in an elementary course of physical chemistry, a large number of concepts and definitions have to be introduced. It is no wonder that students, specially those who are somewhat weak in physics and mathematics, find it difficult to grasp the subject. From our class-room experience with students, we have found that they learn physical chemistry more easily if they solve numerical problems based on the applications of these concepts. Furthermore, the definitions and concepts have to be learnt precisely. And also exercises involving the choice of correct answer from seemingly similar statements definitely sharpens the understanding of the subject.

This book aims at preparing students to learn the basics of physical chemistry through numerical problems and quiz questions. The book is divided into 23 chapters. Each chapter provides brief but sufficient coverage to definit ons of quantities, development of concepts and derivation of important equations. These are further elucidated by suitable solved examples as the subject is developed. This also gives the reader a feeling for the magnitudes of various physico-chemical quantities. A s.t of problems is then included for the sake of practice. Finally, different types of quiz questions (multiple choice type, true or false statements type, and fill in the blanks type) are given so that the student can check if he has really understood the subject. The answers to different types of questions are given at the end of each chapter.

The book encourages the use of SI units. However, it is not uncommon to find data in non-SI units in various university and public examinations. Therefore, we have also given problems based on units other than SI units. We have explained the interconversion of units at the appropriate places.

The book is meant for BSc and BSc (Hons) students of Indian universities. It can also be of use to MSc students and candidates appearing for various public examinations. Suggestions and comments for the improvement of the book by the readers will be most welcome.

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Physico-Chemical Quantities and their Measurements in Physical Chemistry

Physical chemistry deals with the quantitative description of physico-chemical systems. In general such a system can be any part of the universe under study. In practice it consists of matter and/or radiation whose composition and other parameters are independent of time if it is in equilibrium. For a system not in equilibrium these change with time. The system may have boundaries which may be permeable to matter, energy and radiation or to any of their combinations. We shall learn more about these in later chapters. For a system in equilibrium this amounts to the specification of all physico-chemical quantities. These may be measured directly, or derived from other measured quantities. In some cases, they may be calculated theoretically. As the properties of the system are inter-related, it is not necessary to specify all of them for complete characterization. For time dependent systems, evolution in time has to be described. The rate at which they reach the equilibrium state constitutes an important area of physical chemistry.

1.1 UNITS

The measurement and calculation of physico-chemical properties and their interdependence is the essence of physical chemistry. The value of a physical quantity is always equal to the product of a numerical value and a unit. Naturally, we must have a convenient system of units for assigning numerical values to the measured or calculated quantities. Fortunately, it turns out that it is sufficient to define some *basic units* like time, mass, length, etc. Units for other quantities can be derived from these basic units and hence are called *derived units*. In recent years, scientists have generally agreed to the use of SI (Systeme Internationale) units, although a number of units used earlier are still in vogue. In this book we shall mainly use SI units. Problems and examples based exclusively on SI units are preceded by the indication (SI units). However, in view of the use of different types of units during the transition period, it is desirable to know the use of other units, especially their inter-conversion. The factors used in conversion are shown in bold letters to help the readers get acquainted with them.

1.2 SI UNITS

In this system, we define the following basic units:

Mass

The unit of mass is the *kilogram* (kg), defined as the mass of a platinum block stored at the International Bureau of Weights and Measures in France.

Length

The unit of length is the *metre* (m), defined as 1650763.73 wavelengths of the radiation of krypton-86 transition from $2p_{10}$ to $5d_5$, in vacuum.

Time

The unit of time is the *second* (s), defined as 9.192631770×10^9 periods of the radiation of Cs-133 transition between two hyperfine levels of the ground state.

Temperature

The unit of temperature is the *kelvin* (K) defined as the fraction 1/273.15 of the thermodynamic temperature of the triple point of water.

Current

The unit of current is the *ampere* (A) which is equal to the constant current maintained in two straight, parallel conductors of infinite length, and negligible cross section, placed 1 m apart in vacuum, which would produce a force equal to 2×10^{-7} newton per metre.

Amount

The *mole* (mol) is the amount of substance in a system which contains as many elementary entities as there are atoms* in **0.012 kg of carbon—12.**

*The number is equal to the Avogadro number ($N_a = 6.022 \times 10^{23}$).

The elementary entities may be chosen as convenient, not necessarily as physically real individual particles. Thus, we have

n(Cl) — amount of chlorine atoms
n(Cl_2) — amount of chlorine molecules
$n\left(\frac{1}{5}KMnO_4\right)$ – amount of entities $\frac{1}{5}$ $KMnO_4$

For the amount of a substance, we use 'mole' in the text and 'mol' in equations and the symbol for its unit.

When the mole is used, the elementary entities must be specified. They may be atoms, molecules, ions, other particles or specified groups of such particles.

Luminosity

The unit of luminosity is the *candela* (cd), equal to the intensity in the perpendicular direction of the surface of 1/160000 square metres of a black body at the temperature of freezing platinum, under a pressure of 101325 newton per square metre.

Besides the above basic units, we also have the following supplementary SI units:

Plane Angle

The unit of plane angle is the *radian* (rad), equal to the angle between two radii of a circle which cut off, on the circumference, an arc of length equal to the radius.

Solid Angle

The unit of solid angle is the *steradian* (sr) which corresponds to an angle having its vertex at the centre of a sphere and cutting off an area, on the surface of the sphere, equal to that of a square with sides equal to the radius of the sphere.

1.3 DERIVED UNITS

The units of other physical quantities can be derived from the basic units explained above. The names and symbols of some selected quantities are given in Table 1.1

TABLE 1.1 *The Derived SI Units of Some Selected Physical Quantities*

Physical quantity	*Name*	*Symbol for 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	siemens	S	$kg^{-1}\ m^{-2}\ s^3\ A^2 = V^{-1}\ A$
Electric capacitance	farad	F	$A^2\ s^4\ kg^{-1}\ m^{-2} = A\ s\ V^{-1}$
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}

1.4 PREFIXES

The SI units of some of the physical quantities discussed above are either too small or too large. To change the order of magnitude, these are preceded by certain prefixes. With the help of these prefixes it is possible to vary the unit from 10^{-18} to 10^{18}. These are listed in Table 1.2.

TABLE 1.2 *List of Prefixes*

Factor	*Symbol*	*Name*	*Origin*
10^{-1}	d	deci	Latin decimus (ten)
10^{-2}	c	centi	Latin centura (hundred)
10^{-3}	m	milli	Latin milli (thousand)
10^{-6}	μ	micro	Greek micro (small)
10^{-9}	n	nano	Greek nano (dwarf)
10^{-12}	p	pico	Italian pico (small)
10^{-15}	f	femto	Danish femten (fifteen)
10^{-18}	a	atto	Danish atten (eighteen)
10	da	deca	Greek deca (ten)
10^{2}	h	hecto	Greek ekatov (hundred)
10^{3}	k	kilo	Greek kilo (thousand)
10^{6}	M	mega	Greek mega (great)
10^{9}	G	giga	Greek giga (giant)
10^{12}	T	tera	Greek tera (monster)
10^{15}	P	peta	*
10^{18}	E	exa	*

*Tera can be considered to be derived from the tetra *minus* consonant 't' meaning $10^{3\times4} = 10^{12}$. Similarly, if we omit one consonant each from penta, it becomes peta ($10^{3\times5} = 10^{15}$), and hexa becomes exa ($10^{3\times6} = 10^{18}$).

1.5 IMPORTANT NOTES ON THE USE OF SI UNITS

In order to avoid confusion in the use of SI units, it is useful to remember the following:

— Unit combinations should be designated by means of either a dot or leaving space in between, e.g. m.K. (or m K) for metre kelvin and not mK which stands for milli kelvin.

— Words and symbols should not be in mixed forms. Thus, it is not proper to use J per mole; this should be written either as joule per mole or J mol^{-1}. If mathematical operations are indicated, only symbols should be used, e.g. J mol^{-1} and not joules mol^{-1}.

— Exponents also operate on prefixes, e.g.

$$1\ cm^2 = 10^{-4}m^2 \neq 10^{-2}m^2.$$

$$1\ mm^3 = 10^{-9}m^3 \neq 10^{-3}m^3$$

1.6 MICROSCOPIC AND MACROSCOPIC APPROACHES TO PHYSICAL CHEMISTRY

There are two distinct approaches to the study of physical chemistry. In the first, called the *microscopic approach* (or *synthetic approach*), one starts with elementary particles. We first study the properties of atoms and molecules experimentally, by various spectroscopic and diffraction methods, or calculate them theoretically by the method of quantum mechanics. The collection of molecules lead to various states of aggregation like solid, liquid or gas. The properties of these can be calculated, in principle, by the methods of statistical mechanics, if we know the properties of the individual molecules and the nature of the interactions between them. This approach is aesthetically very beautiful and intellectually highly satisfying, but somewhat difficult to the uninitiated as it involves many abstract concepts.

In the second approach, called the *macroscopic approach* (or *analytical approach*), the matter in bulk is subjected to direct observations and the molecular basis of these observations is found. For example, Boyle's law for a gas, established on the basis of p–V measurements at constant temperature, is justified in terms of the kinetic theory of gases postulating that the gas consists of a large number of molecules moving in a random fashion. This approach is easier for the beginner as he can have a direct feeling for the system under investigation. Laws of thermodynamics are applicable to matter in bulk, without regard for structure. Nonetheless, both approaches are intimately connected, and a physical chemist moves back and forth from one approach to the other. Thus, the structure of matter and the energy distribution between molecules leads to a deep understanding of the laws of thermodynamics.

1.7 SOME COMMONLY USED NON-SI UNITS AND THEIR CONVERSION

The use of SI units has been accepted by most of the national and international societies in their publications. Most of the scientific journals recommend the use of SI units and symbols. However, some of the non-SI units (e.g. force, pressure and energy) are still in use. Moreover, physical quantities in older literature are also expressed in such units. It is, therefore, necessary to be familiar with some of the important units and their interconversion.

Force

N	dyn	kg f
1	10^5	0.102
10^{-5}	1	1.02×10^{-6}
9.81	9.81×10^5	1