Physical Chemistry

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Preface

After having taught physical chemistry for many years, we have found that the textbooks available were either too complex without sufficient verbal explanation or lacked the depth and range of topics required for the training of chemists. We therefore set out to write a text that can be easily understood by students who are meeting physical chemistry for the first time and which would still have the mathematical rigor and range necessary for a solid foundation. The students are assumed to have a basic knowledge of chemistry, physics, and mathematics such as is provided by the courses usually given to science students in their first year at a university. Since this book is rather comprehensive, it covers more than can probably be included in a one-year course, and it may be useful in more advanced courses and as a general reference book for those working in fields that require a basic knowledge of the subject.

Several special aids are provided for the student in this book: The *Preview* of each chapter describes the material to be presented in a brief narrative that gives a sense of unity to the material of the chapter. As an aid for the student, all new terms are in *italics* or in **boldface** type for special emphasis. Particular attention should be paid to these terms as well as to the equations that appear in boldface type. There are many worked-out examples in the text in which we have emphasized the dimensionality of the units of the quantities. Key equations that appear in the chapter occur in a concise listing at the end of each chapter. More is said about end-of-chapter material later. A unique feature of this text is Appendix A, in which are listed all the SI quantities and units generally useful to chemists. In addition, the mathematical relationships provided in Appendix C should prove useful as a handy reference.

Organization and Flexibility

We have treated the various branches of physical chemistry in what seems to us to be the most logical order, but this is a matter of personal preference and other teachers may prefer a different order. The book has been written with some flexibility in mind, and it may help if we suggest some alternatives. The subject matter may be divided into the following topics:

A. Chapters 1–6:	General properties of gases, liquids, and solutions; thermodynamics; physical and chemical equilibrium
B. Chapters 7–8:	Electrochemistry of solutions
C. Chapters 9–10:	Chemical kinetics
D. Chapters 11–14:	Quantum chemistry; spectroscopy; statistical mechanics
E. Chapters 15–19:	Some special topics: solids, liquids, surfaces, transport properties, and macromolecules

Our sequence has the advantage that the more difficult topics of Chapters 11–14 can come at the beginning of the second half of the course. The book also lends itself without difficulty to various alternative sequences, such as the following:

A	B	C
Chapters 1–6	Chapters 1–6	Chapters 1–6
Chapters 9–10	Chapters 11–14	Chapters 11–14
Chapters 7–8	Chapters 7–8	Chapters 9–10
Chapters 11–14	Chapters 9–10	Chapters 7–8
Chapters 15–19	Chapters 15–19	Chapters 15–19

Aside from this, the order of topics in some of the sections, such as those in Chapters 15–19, can be easily varied.

End-of-Chapter Material

The *Key Equation* section lists equations with which the student should be thoroughly familiar. This listing should not be construed as including the only equations that are important but rather as foundation expressions that are widely applicable to chemical problems. The *Problems* have been organized according to subject matter and have been graded, the more difficult problems being indicated with an asterisk. The *Supplementary Problems* are generally more difficult and are listed separately. Answers to all problems are included at the back of the book, with detailed solutions provided in a separate *Solutions Manual for Physical Chemistry*.

Units and Symbols

We have tried to adhere strictly to the Système International d' Unités (SI) and to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC); the reader is referred to Appendix A for an outline of these units and recommendations. The essential feature of these recommendations is that the methods of quantity calculus are used; a symbol represents a physical quantity, which is the product of a pure number (the *value* of the quantity) and a unit. Sometimes, as in taking a logarithm or making a plot, one needs the *value* of a quantity, and IUPAC has made no recommendation for a symbol to denote such a value. We have made the innovation of using a superscript *u* (for *unitless*) to denote such a value. For example, the symbol K stands for an equilibrium constant, which in general has units, and we write K^u for the *value* of the equilibrium constant. However, for some of the later topics (e.g., kinetics) we decided that the superscripts complicated the notation unduly, and that by the time these topics were treated the student would understand the point sufficiently well and would not need the help of the superscripts. Thus the logarithm of a rate constant is written simply as ln k, and the reader is to understand that one takes the logarithm of the *value* of k (i.e., of k^u).

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K.J.L.
J.H.M.

TABLE OF RELATIVE ATOMIC MASSES[1]

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	227	Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	[243][2]	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	[237]
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	[210]	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	[249]	Nobelium	No	102	[253]
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	106.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	[242]
Californium	Cf	98	[251]	Polonium	Po	84	210
Carbon	C	6	12.01115	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.907
Cesium	Cs	55	132.905	Promethium	Pm	61	[145]
Chlorine	Cl	17	35.453	Protactinium	Pa	91	231
Chromium	Cr	24	51.996	Radium	Ra	88	226.05
Cobalt	Co	27	58.9332	Radon	Rn	86	222
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96	[247]	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	[254]	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100	[253]	Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	[223]	Silver	Ag	47	107.870
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	[99]
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lr	103	[257]	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	[256]				

[1]Based on Carbon-12.

[2]A value given in brackets is the mass number of the longest-lived or best-known isotope.

THE GREEK ALPHABET

Α, α . . . *Alpha*	Η, η . . . *Eta*	Ν, ν . . . *Nu*	Τ, τ . . . *Tau*
Β, β . . . *Beta*	Θ, ϑ, θ . . *Theta*	Ξ, ξ . . . *Xi*	Υ, υ . . . *Upsilon*
Γ, γ . . . *Gamma*	Ι, ι . . . *Iota*	Ο, ο . . . *Omicron*	Φ, φ, ϕ . . *Phi*
Δ, δ . . . *Delta*	Κ, κ . . . *Kappa*	Π, π . . . *Pi*	Χ, χ . . . *Chi*
Ε, ϵ . . . *Epsilon*	Λ, λ . . . *Lambda*	Ρ, ρ . . . *Rho*	Ψ, ψ . . . *Psi*
Ζ, ζ . . . *Zeta*	Μ, μ . . . *Mu*	Σ, σ . . . *Sigma*	Ω, ω . . . *Omega*

SI PREFIXES

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

SI BASE UNITS

Physical quantity	Symbol for quantity	SI unit	Symbol for unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Thermodynamic temperature	T	kelvin	K
Electric current	I	ampere	A
Luminous intensity	I_v	candela	cd
Amount of substance	n	mole	mol

PHYSICAL CONSTANTS*

Speed of light in vacuum	c	2.998×10^8 m s^{-1}
Elementary charge	e	1.602×10^{-19} C
Avogadro constant	N_A	6.022×10^{23} mol^{-1}
Atomic mass unit	u	1.661×10^{-27} kg
Electron rest mass	m_e	9.100×10^{-31} kg
Proton rest mass	m_p	1.673×10^{-27} kg
Faraday constant	F	9.6485×10^4 C mol^{-1}
Planck constant	h	6.626×10^{-34} J s
Rydberg constant	R_∞	1.097×10^7 m^{-1}
Gas constant	R	8.314 J K^{-1} mol^{-1}
		1.987 cal K^{-1} mol^{-1} dm^3
		0.082 06 dm^3 atm K^{-1} mol^{-1}
Boltzmann constant	k	1.381×10^{-23} J K^{-1}
Permittivity of vacuum	ϵ_0	8.854×10^{-12} C^2 N^{-1} m^2
	$1/4\pi\epsilon_0$	0.8988×10^{10} N m^2 C^{-2}

*More values are given in Appendix B.

NUMERICAL CONSTANTS

$\pi = 3.141\ 592\ 65$
$e = 2.718\ 281\ 828$
$\ln x = \log x / \log e = 2.302\ 585\ 09 \log x$

OTHER UNITS

Quantity	Symbol for Quantity	SI Unit and Symbol	Other Units
Length	l	metre (m)	1 angstrom (Å) $= 10^{-10}$ m = 0.1 nm; 1 micron $= 10^{-6}$ m (not recommended)
Volume	V	cubic metre (m^3)	1 liter = 1 dm^3 (by definition)
Mass	m	kilogram (kg)	
Time	t	second (s)	1 min = 60 s; 1 year $= 3.156 \times 10^7$ s
Frequency	ν	hertz (Hz $\equiv s^{-1}$)	
Temperature	T	kelvin (K)	$\theta/°C = T/K - 273.15$
Electric current	I	ampere (A)	
Electric charge	Q	coulomb (C ≡ A s)	1 esu $= 3.336 \times 10^{-10}$ C
Electric potential	V, ϕ	volt (V $\equiv$ kg m^2 s^{-3} A^{-1})	
Electric resistance	R	ohm (Ω $\equiv$ V A^{-1})	
Electric capacitance	C	farad (F $\equiv$ C V^{-1})	
Force	F	newton (N $\equiv$ kg m s^{-2})	1 dyne $= 10^{-5}$ N
Pressure	P	pascal (Pa $\equiv$ kg m^{-1} s^{-2})	1 atm $= 1.01325 \times 10^5$ Pa; 1 bar $= 10^5$ Pa; 1 torr = 1mmHg = 133.322 Pa
Energy	E, U	joule (J $\equiv$ kg m^2 s^{-2})	1 erg $= 10^{-7}$ J; 1 cal = 4.184 J (by definition); 1 electron volt (eV) $= 1.602 \times 10^{-19}$ J $= 96.47$ kJ mol^{-1} $= 23.06$ kcal mol^{-1}; 1 atm dm^3 = 101.325 J = 24.22 cal
Power	P	watt (W $\equiv$ J s^{-1})	

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