PHYSICAL CHEMISTRY

Robert A. Alberty

Robert J. Silbey

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PHYSICAL CONSTANTS[a]

Speed of light in vacuum	c	$2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}$
Elementary charge	e	$1.602 \times 10^{-19}\ \mathrm{C}$
Avogadro constant	N_{A}	$6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
Atomic mass unit	u	$1.661 \times 10^{-27}\ \mathrm{kg}$
Electron rest mass	m_{e}	$9.100 \times 10^{-31}\ \mathrm{kg}$
Proton rest mass	m_{p}	$1.673 \times 10^{-27}\ \mathrm{kg}$
Faraday constant	F	$9.6485 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
		$23,060\ \mathrm{cal\ mol^{-1}\ eV^{-1}}$
Planck constant	h	$6.626 \times 10^{-34}\ \mathrm{J\ s}$
Rydberg constant	R_{∞}	$1.097 \times 10^{7}\ \mathrm{m^{-1}}$
Gas constant	R	$8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$
		$0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}}$
		$1.987\ \mathrm{cal\ K^{-1}\ mol^{-1}}$
		$0.082\,06\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$
Boltzmann constant	k	$1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
Permittivity of vacuum	ϵ_0	$8.854 \times 10^{-12}\ \mathrm{C^{2}\ N^{-1}\ m^{-2}}$
	$1/4\pi\epsilon_0$	$0.8988 \times 10^{10}\ \mathrm{N\ m^{2}\ C^{-2}}$

[a] The current best values and their uncertainties are given in Appendix B.

SOME NUMERICAL CONSTANTS AND CONVERSION FACTORS

$\pi = 3.141\,592\,65$

$e = 2.718\,281\,828$

$\ln x = \log x / \log e = 2.302\,585\,09 \log x$

$101\,325\ \mathrm{N\ m^{-2}\ atm^{-1}}$

$10^{5}\ \mathrm{N\ m^{-2}\ bar^{-1}}$

$1.01325\ \mathrm{bar\ atm^{-1}}$

$2.54\ \mathrm{cm\ inch^{-1}}$

$453.6\ \mathrm{g\ lb^{-1}}$

$4.184\ \mathrm{J\ cal^{-1}}$

$1.602 \times 10^{-19}\ \mathrm{J\ eV^{-1}}$

$10^{-3}\ \mathrm{m^{3}\ L^{-1}}$

$133.32\ \mathrm{Pa\ torr^{-1}}$

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

TABLE OF RELATIVE ATOMIC MASSES 1987[a]

Scaled to the relative atomic mass, $A_r(^{12}\mathrm{C}) = 12$

Values given here apply to elements as they exist naturally on Earth. The uncertainties in the values are indicated by the figures given in parentheses, which is applicable to the last digit.

Atomic Number	Name	Symbol	Relative Atomic Mass	Atomic Number	Name	Symbol	Relative Atomic Mass
1	Hydrogen	H	1.007 94(7)	55	Cesium	Cs	132.905 43(5)
2	Helium	He	4.002 602(2)	56	Barium	Ba	137.327(7)
3	Lithium	Li	6.941(2)	57	Lanthanum	La	138.905 5(2)
4	Beryllium	Be	9.012 182(3)	58	Cerium	Ce	140.115(4)
5	Boron	B	10.811(5)	59	Praseodymium	Pr	140.907 65(3)
6	Carbon	C	12.011(1)	60	Neodymium	Nd	144.24(3)
7	Nitrogen	N	14.006 74(7)	61	Promethium	Pm	
8	Oxygen	O	15.999 4(3)	62	Samarium	Sm	150.36(3)
9	Fluorine	F	18.998 403 2(9)	63	Europium	Eu	151.965(9)
10	Neon	Ne	20.179 7(6)	64	Gadolinium	Gd	157.25(3)
11	Sodium	Na	22.989 768(6)	65	Terbium	Tb	158.925 34(3)
12	Magnesium	Mg	24.305 0(6)	66	Dysprosium	Dy	162.50(3)
13	Aluminum	Al	26.981 539(5)	67	Holmium	Ho	164.930 32(3)
14	Silicon	Si	28.085 5(3)	68	Erbium	Er	167.26(3)
15	Phosphorus	P	30.973 762(4)	69	Thulium	Tm	168.934 21(3)
16	Sulfur	S	32.066(6)	70	Ytterbium	Yb	173.04(3)
17	Chlorine	Cl	35.452 7(9)	71	Lutetium	Lu	174.967(1)
18	Argon	Ar	39.948(1)	72	Hafnium	Hf	178.49(2)
19	Potassium	K	39.098 3(1)	73	Tantalum	Ta	180.947 9(1)
20	Calcium	Ca	40.078(4)	74	Tungsten	W	183.85(3)
21	Scandium	Sc	44.955 910(9)	75	Rhenium	Re	186.207(1)
22	Titanium	Ti	47.88(3)	76	Osmium	Os	190.2(1)
23	Vanadium	V	50.941 5(1)	77	Iridium	Ir	192.22(3)
24	Chromium	Cr	51.996 1(6)	78	Platinum	Pt	195.08(3)
25	Manganese	Mn	54.938 05(1)	79	Gold	Au	196.966 54(3)
26	Iron	Fe	55.847(3)	80	Mercury	Hg	200.59(3)
27	Cobalt	Co	58.933 20(1)	81	Thallium	Tl	204.383 3(2)
28	Nickel	Ni	58.69(1)	82	Lead	Pb	207.2(1)
29	Copper	Cu	63.546(3)	83	Bismuth	Bi	208.980 37(3)
30	Zinc	Zn	65.39(2)	84	Polonium	Po	
31	Gallium	Ga	69.723(1)	85	Astatine	At	
32	Germanium	Ge	72.61(2)	86	Radon	Rn	
33	Arsenic	As	74.921 59(2)	87	Francium	Fr	
34	Selenium	Se	78.96(3)	88	Radium	Ra	
35	Bromine	Br	79.904(1)	89	Actinium	Ac	
36	Krypton	Kr	83.80(1)	90	Thorium	Th	232.038 1(1)
37	Rubidium	Rb	85.467 8(3)	91	Protactinium	Pa	
38	Strontium	Sr	87.62(1)	92	Uranium	U	238.028 9(1)
39	Yttrium	Y	88.905 85(2)	93	Neptunium	Np	
40	Zirconium	Zr	91.224(2)	94	Plutonium	Pu	
41	Niobium	Nb	92.906 38(2)	95	Americium	Am	
42	Molybdenum	Mo	95.94(1)	96	Curium	Cm	
43	Technetium	Tc		97	Berkelium	Bk	
44	Ruthenium	Ru	101.07(2)	98	Californium	Cf	
45	Rhodium	Rh	102.905 50(3)	99	Einsteinium	Es	
46	Palladium	Pd	106.42(1)	100	Fermium	Fm	
47	Silver	Ag	107.868 2(2)	101	Mendelevium	Md	
48	Cadmium	Cd	112.411(8)	102	Nobelium	No	
49	Indium	In	114.82(1)	103	Lawrencium	Lr	
50	Tin	Sn	118.710(7)	104	Unnilquadium	Unq	
51	Antimony (Stibium)	Sb	121.75(3)	105	Unnilpentium	Unp	
52	Tellurium	Te	127.60(3)	106	Unnilhexium	Unh	
53	Iodine	I	126.904 47(3)	107	Unnilseptium	Uns	
54	Xenon	Xe	131.29(2)				

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[a] IUPAC Commission on Atomic Weights, *J. Phys. Chem. Ref. Data*, **17**:1791 (1988).

Preface

The objective of this book is to make the concepts and methods of physical chemistry clear and interesting to students who have had a year of calculus and a year of physics. The underlying theory of chemical phenomena is complicated, and so it is a challenge to make the most important concepts and methods understandable to undergraduate students. However, these basic ideas are accessible to students, and they will find them useful whether they are chemistry majors, biologists, engineers, or earth scientists. The basic theory of chemistry is presented from the viewpoint of academic physical chemists, but many applications of physical chemistry to practical problems are described.

A course in physical chemistry provides many opportunities for the immediate application of ideas and equations in solving problems. In this edition, the number of examples has been increased to 244, which is 34 percent greater than the previous, seventh, edition. In addition, many calculations are carried out in the body of the text. The number of figures has been increased to 356, (30% greater than the previous edition). The number of problems is essentially the same as in the seventh edition, but 26 percent of the old problems have been replaced. There are also two parallel sets of problems at the end of each chapter. The answers for the first set are given in the Appendix. The *Solutions Manual for Physical Chemistry* contains worked-out solutions for all of the problems in the first set and answers for the second set.

As a new feature in this edition, we have discussed one or two Special Topics at the end of each chapter.

Since the number of credits in physical chemistry courses, and therefore the need for more advanced material, varies at different universities and colleges, more topics have been included in this edition than can be covered in some courses.

The book is still divided into four parts, but they have been reorganized since the seventh edition. The book starts with thermodynamics to show clearly the power and limits of this treatment of equilibrium. In general, the treatment of thermodynamics has been upgraded. There is a more systematic treatment of the second law and more emphasis on the entropy. There is also emphasis on the solution of problems in chemical equilibrium, and the material on electrochemical equilibria has been revised extensively to make it clearer. In addition, the thermodynamic tables in the Appendix have been brought up to date. Finally, the difference between extensive thermodynamic quantities and molar thermodynamic quantities has been clarified by using overbars on the molar thermodynamic quantities (see the Note to Students).

Part II, on quantum mechanics and spectroscopy, describes the behavior of atoms and molecules. The level of the treatment of quantum mechanics has been raised again because of its central importance for understanding modern physical chemistry. Linear operators, eigenvectors, and eigenvalues are introduced early and used throughout. Emphasis is placed on the description of molecular properties and spectroscopy using quantum mechanical ideas.

In Part III, Statistical Mechanics and Kinetics, the chapter on Statistical Mechanics has been completely rewritten to make this subject more understandable and usable to students. Theoretical gas kinetics has been combined with photochemistry to form a new chapter, Chemical Dynamics and Photochemistry.

Part IV, Macroscopic and Microscopic Structures, contains two new chapters on Macromolecules and Surface Dynamics, respectively, that provide increased emphasis on these two important subject areas.

Throughout, we have emphasized the use of SI (Système International d'Unités) units, although some other units are used when they are especially convenient or widely used. The advantage of SI is that it is coherent: when SI units are used in a calculation, the result comes out in SI units without any numerical factors. This feature of SI is particularly important in physical chemistry, which uses such a wide range of physical quantities. The underlying unity of science is emphasized by the use of seven base units to represent all physical quantities. The Appendix contains a list of Symbols for Physical Quantities, their SI units, and the numbers of the Sections where they are introduced. The fundamental physical constants of this edition are from the 1986 report of the CODATA Task Group on Fundamental Constants.

History

Outlines of Theoretical Chemistry, as it was then entitled, was written in 1913 by Frederick Getman, who carried it through 1927 in four editions. The next four editions were written by Farrington Daniels. In 1955, Robert Alberty joined Farrington Daniels, the name of the book was changed to *Physical Chemistry*, and the numbering of the editions was started over. Their collaboration ended in 1972 when Farrington Daniels died. After seven editions, the current senior author welcomes Robert J. Silbey as coauthor. Robert J. Silbey has a well-deserved reputation as an excellent teacher, and he brings a broad experience in physical chemistry to this book, which again is a first edition. It is remarkable that this textbook of *Physical Chemistry* traces its origins back 78 years.

Over the years this book has profited tremendously from the advice of physical chemists all over the world. Many physical chemists who care how their subject is presented have written to us with their comments, and we hope that will continue. We are especially indebted to our colleagues at MIT who have reviewed sections of this editions and have given us the benefit of their advice. These include Sylvia T. Ceyer, Carl W. Garland, Irwin Oppenheim, and Mark S. Wrighton. Parts of the book were reviewed by members of IUPAC Commission I.1 on Physiochemical Symbols, Terminology, and Units, including I. Mills, T. Cvitas, N. Kallay, R. Cohen, and B. Holmstrom. Important advice was also provided by A. J. Bard, M. Chase, R. Parsons, P. Rieger, and R. Sauer.

R. D. Allendoerfer (SUNY University at Buffalo), D. W. Beistel (University of Missouri-Rolla), T. M. Dunn (University of Michigan), R. F. Firestone (Ohio State University), N. Ganapathisubramaninian (Wake Forest), D. K. Gosser (The City College of CUNY), R. C. Millikan (University of California-Santa Barbara), M. O'Keeffe (Arizona State University), J. W. Reed (Kent State University), J. H. Reeves (Wilmington, North Carolina), S. L. Seager (Weber

State College), D. F. Tuan (Kent State University), and S. Widmer (Adelphi University) read parts of this edition and made many useful suggestions.

We are indebted to John Wiley for its support, and especially to our editors, Dennis Sawicki and Nedah Rose, for their advice.

We are also indebted to Lillian Alberty and Vera Spanos for the difficult job of typing the manuscript.

Cambridge, Massachusetts
January, 1991

Robert A. Alberty
Robert J. Silbey

Note to Students

In this book we will discuss over 300 physical quantities. All are listed in Appendix F, with the section numbers where they are defined. The value of a physical quantity is equal to the product of a numerical factor and a unit:

$$\text{physical quantity} = \text{numerical value} \times \text{unit}$$

The values of all physical quantities can be expressed in terms of SI base units (see Appendix A), but some physical quantities are dimensionless, and so the symbol for the SI unit is taken as 1 because this is what you get when units cancel.

Certain combinations of base units are used so frequently that they are given special symbols. For example, the base unit $\mathrm{kg\ m^2\ s^{-2}}$ for energy is represented by J, the joule, named in honor of Joule.

Note that in print, physical quantities are represented by italic type and units are represented by roman type. Physical quantities that are vectors or matrices are represented by boldface italic type.

The SI system of units has the advantage that it is *coherent*. This means that in using an equation that gives a relationship between physical quantities, if all quantities in a calculation are expressed in SI base units, the result will be expressed in SI base units without including any numerical factors. This is very helpful in physical chemistry where physical quantities from quite different areas of science come together in the same equation. However, for reasons of convenience and history, some non-SI units are used in physical chemistry. They can each be expressed in terms of SI units, and a list of them is given in the Appendix A.

At equilibrium, a system has certain extensive properties, including volume (V), internal energy (U), enthalpy (H), entropy (S), Helmholtz energy (A), and Gibbs energy (G). These physical quantities are extensive because their values depend on the size of the system. If the volume of a system is divided by the amount of substance n, we obtain the molar volume $\overline{V} = V/n$. The molar volume is an intensive quantity because its value does not depend on the size of the system (Section 1.1). The molar volume has the SI units $\mathrm{m^3\ mol^{-1}}$. In a similar way we can define intensive quantities $\overline{U}$, $\overline{H}$, $\overline{S}$, $\overline{A}$, and $\overline{G}$, known as the molar internal energy, and so on. The SI unit of a molar quantity always includes $\mathrm{mol^{-1}}$.

A subscript i on a molar quantity or a chemical formula in parenthesis is used to identify the substance, as in $\overline{V}_i$ or $\overline{V}(i)$. These symbols are also used to represent partial molar quantities (Section 4.12). When it is important to emphasize that we are dealing with a pure substance, a superscript * is used as in $\overline{V}_i^*$ for the molar volume of a pure substance or P_i^* for the vapor pressure of a pure substance.

When a system is in its standard state, the thermodynamic property has a superscript degree sign, as in H°, S°, or G°. The molar property of a substance in its standard state is represented, for example, by $\overline{H}_i^\circ$, $\overline{S}_i^\circ$, and $\overline{G}_i^\circ$. Actually, it is not possible to determine the absolute values of the internal energy, enthalpy, Helmholtz energy, and Gibbs energy, and so the values of these properties are determined relative to those of the elements. In particular, we will make a good deal of use of the standard molar enthalpy of formation $\Delta_f H_i^\circ$ and the standard molar Gibbs energy of formation $\Delta_f G_i^\circ$. The overbar is not used on these quantities because the Δ_f indicates the formation of one mole of i from the elements contained in it. The formation quantities necessarily have mol^{-1} in their units.

Other Δ quantities that are frequently used are $\Delta_{\text{mix}}S$, $\Delta_{\text{mix}}V$, $\Delta_{\text{fus}}H$, $\Delta_{\text{vap}}H$, and $\Delta_r G^\circ$. These symbols are used to represent molar quantities and, again, the overbar is not used. The units for these quantities necessarily include mol^{-1}.

Recommendations of the International Union of Pure and Applied Chemistry on these matters are given in I. Mills, *Quantitative, Units, and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Oxford, 1988.

A problem book containing worked-out solutions for the first set of problems and answers for the second set of problems is available as a companion to this text. Please ask for *Solutions Manual for Physical Chemistry*, by Robert A. Alberty and Robert J. Silbey.

PHYSICAL CHEMISTRY

ENERGY CONVERSION FACTORS[a]

	cm^{-1}	MHz	aJ	eV	E_h	kJ/mol	kcal/mol	K
1 cm^{-1} =	1.00000000E00	2.99792458E04	1.98644746E-05	1.23984245E-04	4.55633530E-06	1.19626582E-02	2.85914392E-03	1.43876866E00
1 MHz =	3.33564095E-05	1.00000000E00	6.62607550E-10	4.13566924E-09	1.51982986E-10	3.99031324E-07	9.53707754E-08	4.79921566E-05
1 aJ =	5.03411250E04	1.50918896E09	1.00000000E00	6.24150636E00	2.29371045E-01	6.02213670E02	1.43932522E02	7.24292330E04
1 eV =	8.06554093E03	2.41798834E08	1.60217733E-01	1.00000000E00	3.67493088E-02	9.64853090E01	2.30605423E01	1.16044475E04
1 E_h =	2.19474629E05	6.57968386E09	4.35974820E00	2.72113961E01	1.00000000E00	2.62549996E03	6.27509552E02	3.15773218E05
1 kJ/mol =	8.35934612E01	2.50606892E06	1.66054019E-03	1.03642721E-02	3.80879838E-04	1.00000000E00	2.39005736E-01	1.20271652E02
1 kcal/mol =	3.49755041E02	1.04853924E07	6.94770014E-03	4.33641146E-02	1.59360124E-03	4.18400000E00	1.00000000E00	5.03216592E02
1 K =	6.95038770E-01	2.08367381E04	1.38065800E-05	8.61738569E-05	3.16682968E-06	8.31451121E-03	1.98721587E-03	1.00000000E00

[a] When a physical quantity is expressed in the units in the left column, the factor is the number to multiply by to convert to the units at the head of the column.

RELATIVE ATOMIC MASSES AND ISOTOPIC ABUNDANCES[a,b]

Z	Symbol	A	Relative Atomic Mass, m_a/u	Isotopic Abundance, x/%
1	H	1	1.007 825 037(10)	99.985(1)
		2	2.014 101 787(21)	0.015(1)
		3*	3.016 049 286(32)	
2	He	3	3.016 029 297(33)	0.000 138(3)
		4	4.002 603 25(5)	99.999 862(3)
3	Li	6	6.015 123 2(8)	7.5(2)
		7	7.016 004 5(9)	92.5(2)
4	Be	9	9.012 182 5(4)	100
5	B	10	10.012 938 0(5)	19.9(2)
		11	11.009 305 3(5)	80.1(2)
6	C	12	12 (by definition)	98.90(3)
		13	13.003 354 839(17)	1.10(3)
		14*	14.003 241 993(24)	
7	N	14	14.003 074 008(23)	99.634(9)
		15	15.000 108 978(38)	0.366(9)
8	O	16	15.994 914 64(5)	99.762(15)
		17	16.999 130 6(8)	0.038(3)
		18	17.999 159 39(32)	0.200(12)
9	F	19	18.998 403 25(14)	100
10	Ne	20	19.992 439 1(5)	90.51(9)
		21	20.993 845 3(12)	0.27(2)
		22	21.991 383 7(6)	9.22(9)
11	Na	23	22.989 769 7(9)	100
12	Mg	24	23.985 045 0(8)	78.99(3)
		25	24.985 839 2(12)	10.00(1)
		26	25.982 595 4(10)	11.01(2)
13	Al	27	26.981 541 3(7)	100
14	Si	28	27.976 928 4(7)	92.23(1)
		29	28.976 496 4(9)	4.67(1)
14	Si	30	29.973 771 7(10)	3.10(1)
15	P	31	30.975 363 8(11)	100
16	S	32	31.972 071 8(6)	95.02(9)
		33	32.971 459 1(8)	0.75(1)
		34	33.967 867 74(29)	4.21(8)
		36	35.967 079 0(16)	0.02(1)
17	Cl	35	34.968 852 729(68)	75.77(5)
		37	36.965 902 62(11)	24.23(5)
35	Br	79	78.918 336 1(38)	50.69(5)
		81	80.916 290(6)	49.31(5)
53	I	127	126.904 477(5)	100

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[a] IUPAC Commission on Atomic Weights, *Pure Appl. Chem.* **56**:653 (1984).

[b] An asterisk denotes an unstable nuclide. The standard error in parentheses is applicable to the last digits quoted.

Contents

PART ONE
THERMODYNAMICS

Thermodynamics deals with the interconversion of various kinds of energy and the changes in physical properties that are involved. Thermodynamics is concerned with equilibrium states of matter and has nothing to do with time. Even so, it is one of the most powerful tools of physical chemistry; because of its importance, the first part of this book is devoted to it. The first law of thermodynamics deals with the amount of work that can be done by a chemical or physical process and the amount of heat that is absorbed or evolved. On the basis of the first law it is possible to build up tables of enthalpies of formation that may be used to calculate enthalpy changes for reactions that have not yet been studied. With information on heat capacities of reactants and products also available, it is possible to calculate the heat of a reaction at a temperature where it has not previously been studied.

The second law of thermodynamics deals with the natural direction of processes and the question of whether a given chemical reaction can occur by itself. The second law was formulated initially in terms of the efficiencies of heat engines, but it also leads to the definition of entropy, which is important in determining the direction of chemical change. The second law provides the basis for the definition of the equilibrium constant for a chemical reaction. It provides an answer to the question, "To what extent will this particular reaction go before equilibrium is reached?" It also provides the basis for reliable predictions of the effects of temperature, pressure, and concentration on chemical and physical equilibrium. The third law provides the basis for calculating equilibrium constants from calorimetric measurements only. This is an illustration of the way in which thermodynamics interrelates apparently unrelated measurements on systems at equilibrium.

After discussing the laws of thermodynamics and the various physical quantities it involves, our first applications will be to the quantitative treatment of chemical equilibrium. These methods are then applied to equilibrium between different phases. This provides the basis for the quantitative treatment of distillation and for the interpretation of the phase changes in mixtures of solids. Then thermodynamics is applied to electrochemical cells and biochemical reactions.