WALLACE S. BREY, Jr.

PRINCIPLES of
PHYSICAL CHEMISTRY

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An Introduction to Their Use
in the Biological Sciences

by

WALLACE S. BREY, Jr.

University of Florida

New York

APPLETON-CENTURY-CROFTS, INC.

PERIODIC CLASSIFICATION OF THE ELEMENTS

The atomic number is given above the symbol of the element; the atomic weight, to no more than four significant figures, below the symbol.

PERIODS	Group→	I$_a$	II$_a$	III$_b$	IV$_b$	V$_b$	VI$_b$	VII$_b$	VIII$_b$			I$_b$	II$_b$	III$_a$	IV$_a$	V$_a$	VI$_a$	VII$_a$	VIII$_a$
1		1 H 1.008																	2 He 4.003
2		3 Li 6.940	4 Be 9.013											5 B 10.82	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3		11 Na 22.99	12 Mg 24.32											13 Al 26.98	14 Si 28.09	15 P 30.98	16 S 32.07	17 Cl 35.46	18 A 39.94
4		19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.92	36 Kr 83.80
5		37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6		55 Cs 132.9	56 Ba 137.4	57* La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210	85 At (210)	86 Rn 222
7		87 Fr (223)	88 Ra 226.1	89† Ac 227															

* Lantharide → Elements 58–71	58 Ce 140.1	59 Pr 140.9	60 Nd 144.3	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
† Actinide → Elements 90–101	90 Th 232.1	91 Pa 231	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (245)	97 Bk (249)	98 Cf (249)	99 E (253)	100 Fm (254)	101 Mv (256)		

COMMON LOGARITHMS

n	0	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117
41	6128	6138	6149	6160	6170	7180	6191	6201	6212	6222
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396
n	0	1	2	3	4	5	6	7	8	9

Prop. Parts

	43	42	41	40
1	4.3	4.2	4.1	4.0
2	8.6	8.4	8.2	8.0
3	12.9	12.6	12.3	12.0
4	17.2	16.8	16.4	16.0
5	21.5	21.0	20.5	20.0
6	25.8	25.2	24.6	24.0
7	30.1	29.4	28.7	28.0
8	34.4	33.6	32.8	32.0
9	38.7	37.8	36.9	36.0

	39	38	37	36
1	3.9	3.8	3.7	3.6
2	7.8	7.6	7.4	7.2
3	11.7	11.4	11.1	10.8
4	15.6	15.2	14.8	14.4
5	19.5	19.0	18.5	18.0
6	23.4	22.8	22.2	21.6
7	27.3	26.6	25.9	25.2
8	31.2	30.4	29.6	28.8
9	35.1	34.2	33.3	32.4

	35	34	33	32
1	3.5	3.4	3.3	3.2
2	7.0	6.8	6.6	6.4
3	10.5	10.2	9.9	9.6
4	14.0	13.6	13.2	12.8
5	17.5	17.0	16.5	16.0
6	21.0	20.4	19.8	19.2
7	24.5	23.8	23.1	22.4
8	28.0	27.2	26.4	25.6
9	31.5	30.6	29.7	28.8

	31	30	29	28
1	3.1	3.0	2.9	2.8
2	6.2	6.0	5.8	5.6
3	9.3	9.0	8.7	8.4
4	12.4	12.0	11.6	11.2
5	15.5	15.0	14.5	14.0
6	18.6	18.0	17.4	16.8
7	21.7	21.0	20.3	19.6
8	24.8	24.0	23.2	22.4
9	27.9	27.0	26.1	25.2

	27	26	25	24
1	2.7	2.6	2.5	2.4
2	5.4	5.2	5.0	4.8
3	8.1	7.8	7.5	7.2
4	10.8	10.4	10.0	9.6
5	13.5	13.0	12.5	12.0
6	16.2	15.6	15.0	14.4
7	18.9	18.2	17.5	16.8
8	21.6	20.8	20.0	19.2
9	24.3	23.4	22.5	21.6

COMMON LOGARITHMS

n	0	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996
n	0	1	2	3	4	5	6	7	8	9

Prop. Parts

	23	22	21	20
1	2.3	2.2	2.1	2.0
2	4.6	4.4	4.2	4.0
3	6.9	6.6	6.3	6.0
4	9.2	8.8	8.4	8.0
5	11.5	11.0	10.5	10.0
6	13.8	13.2	12.6	12.0
7	16.1	15.4	14.7	14.0
8	18.4	17.6	16.8	16.0
9	20.7	19.8	18.9	18.0

	19	18	17	16
1	1.9	1.8	1.7	1.6
2	3.8	3.6	3.4	3.2
3	5.7	5.4	5.1	4.8
4	7.6	7.2	6.8	6.4
5	9.5	9.0	8.5	8.0
6	11.4	10.8	10.2	9.6
7	13.3	12.6	11.9	11.2
8	15.2	14.4	13.6	12.8
9	17.1	16.2	15.3	14.4

	15	14	13	12
1	1.5	1.4	1.3	1.2
2	3.0	2.8	2.6	2.4
3	4.5	4.2	3.9	3.6
4	6.0	5.6	5.2	4.8
5	7.5	7.0	6.5	6.0
6	9.0	8.4	7.8	7.2
7	10.5	9.8	9.1	8.4
8	12.0	11.2	10.4	9.6
9	13.5	12.6	11.7	10.8

	11	10	9	8
1	1.1	1.0	0.9	0.8
2	2.2	2.0	1.8	1.6
3	3.3	3.0	2.7	2.4
4	4.4	4.0	3.6	3.2
5	5.5	5.0	4.5	4.0
6	6.6	6.0	5.4	4.8
7	7.7	7.0	6.3	5.6
8	8.8	8.0	7.2	6.4
9	9.9	9.0	8.1	7.2

	7	6	5	4
1	0.7	0.6	0.5	0.4
2	1.4	1.2	1.0	0.8
3	2.1	1.8	1.5	1.2
4	2.8	2.4	2.0	1.6
5	3.5	3.0	2.5	2.0
6	4.2	3.6	3.0	2.4
7	4.9	4.2	3.5	2.8
8	5.6	4.8	4.0	3.2
9	6.3	5.4	4.5	3.6

Prop. Parts

PRINCIPLES of
PHYSICAL CHEMISTRY

TEXTS IN CHEMISTRY

Ralph S. Halford, *Columbia University*
CONSULTING EDITOR

PREFACE

This book is intended to acquaint the biological scientist with the field of physical chemistry and to indicate how the understanding of physico-chemical principles sheds light on the behavior of matter. In addition to the fundamental principles of the subject, there are also presented some illustrations of the application of physical chemistry to the solution of biochemical problems.

The mathematical background required of the reader is limited to simple algebra and the use of logarithms. Although some ideas of the calculus are introduced where appropriate to the development of the subject, these are fully explained as they are employed. A brief mathematical appendix summarizes pertinent mathematical principles.

It is expected that the book will serve as a text for a one-semester course for premedical students, such as the author has taught for a number of years in three different institutions. Enough material has been included, however, so that it will be adequate for a full year's course, while for one semester's work the instructor has the opportunity to make a selection from among the subject matter in the latter chapters.

Experienced workers in the biological and biochemical fields may find the book useful as a review of basic principles and as an introduction to some unfamiliar areas. To this end, the author has endeavored to make the discussions of fundamental ideas sufficiently complete so that they may be of value to the independent reader, and to supply in the bibliographies a guide to helpful supplemental information to be found in the literature at various levels of specialization, from the elementary introduction to the advanced treatment appropriate for someone who wishes to undertake research in a particular field.

Finally, it is a pleasure to express my appreciation for assistance in the preparation of the manuscript to my wife, Mary Louise. Her aid, encouragement, and constructive criticism have contributed materially to the writing of the book.

Gainesville, Florida

W. S. B., Jr.

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CONTENTS

1 STATES OF MATTER

1.1 INTRODUCTION

Molecular picture of matter

The differences that we observe in the characteristics of the three states of matter—gas, liquid, and solid—depend upon variations in the condition of aggregation of the molecules of which matter is composed. In a gas, the molecules are relatively far apart and are free to move almost independently of one another. The *kinetic theory* describes the molecules of gases as separate particles which are in continuous motion. Each molecule travels in a straight line until it collides with another molecule or strikes the wall of the vessel in which it is confined. When the confining vessel is enlarged, molecular motion causes the gas to spread through all of the newly accessible space, whereas external application of pressure readily compresses the gas into a smaller volume, for the molecules have a relatively large amount of empty space between them.

In a liquid, the molecules are more restricted in their movements; they are able to roll past one another so that the liquid can flow, but they detach themselves from intimate association with other molecules in the bulk of the liquid only with considerable difficulty. In a solid, each molecule has a definitely assigned average position, about which it may vibrate; movement of the molecule out of its own small compartment, formed by neighboring molecules, is a comparatively unusual event.

The state assumed by a particular sample of matter under a given set of conditions depends upon a balance between the kinetic energy of the molecules, on the one hand, and the sum of the intermolecular attractive forces plus the restraining effect, or pressure, imposed by the environment, on the other hand. The average kinetic energy per molecule in a group of molecules increases as the absolute temperature increases. In fact, a rise in temperature is essentially an increase in molecular activity resulting from the addition of energy: for gaseous molecules the velocity of translational motion increases, whereas in a solid the vibratory motion becomes greater in magnitude.
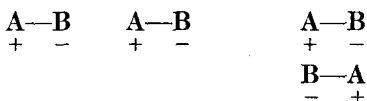
At a sufficiently low temperature any material will be a solid; let us now picture what happens as the temperature of the material is raised. The molecules acquire additional energy, and eventually the amount of this

1

energy is sufficient to disrupt the solid structure and to permit the molecules to leave their localized positions. At this temperature there occurs fusion, or melting, of the solid to form liquid. Further increase in temperature of the liquid decreases its resistance to flow, or viscosity, and there is finally reached a temperature at which another change of state occurs, the formation of a vapor. Vaporization requires energy sufficient both to pull the molecules away from one another against the forces of attraction which hold them together in the liquid, and to do the work of pushing back the atmosphere or the surrounding container to permit the very large volume change associated with conversion of liquid to gas.
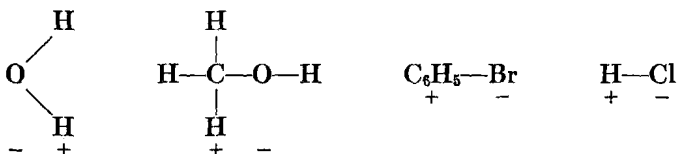
Intermolecular forces

The nonchemical forces, often referred to as *van der Waals forces*, by which atoms or molecules attract one another, are primarily electrical in nature, the attraction of positive charges for negative charges. Despite the fact that an atom or molecule when viewed from a distance is electrically neutral, an observer close to the particle may find himself nearer to the charge of one sign than to that of the opposite sign. As a consequence of their origin, van der Waals forces are then very short range forces.

Molecules are composed of atoms, each of which consists of a positive nucleus and negative electrons moving about outside the nucleus. In forming a molecule the constituent atoms share some of their electrons, which are then able to move about in the vicinity of two or more different atoms. If the "center of gravity" of the negative charges carried by the electrons does not, in a certain molecule, coincide with the center of gravity of the positive charges resident on all the atomic nuclei, that molecule is said to have a separation of charge, or a *dipole*. When two particles having dipoles meet with appropriate orientation, either end-to-end or side-by-side, they attract one another:

$$
\begin{array}{ccccc}
\text{A—B} & & \text{A—B} & & \text{A—B} \\
+ \quad - & & + \quad - & & + \quad - \\
& & & & \text{B—A} \\
& & & & - \quad +
\end{array}
$$

In some molecules, a dipole is a permanent feature of the structure as a consequence of differing affinities of unlike atoms for the valence electrons. These unequal forces pull the electrons toward one part of the molecule. There are, for example, permanent dipoles in water, methanol, bromobenzene, and gaseous hydrogen chloride molecules:

$$
\begin{array}{cccc}
\overset{\displaystyle\text{H}}{\underset{\displaystyle\text{H}}{\diagup\!\!\!\!\!\diagdown}}\!\!\text{O} &
\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—O—H} &
C_6H_5\text{—Br} &
\text{H—Cl}
\end{array}
$$

In other molecules—even in monatomic molecules—which do not them-
selves have a permanent dipole, a temporary charge-separation or induced
dipole may be produced on approach of another molecule which has a
permanent dipole. The direction of the *induced dipole* is always that which
causes attraction to the inducing dipole. Consider as a nonpolar particle
the helium atom, and as the approaching polar molecule a water mole-
cule. If the negative end of the water molecule approaches the helium atom,
it repels electrons from the portion of the atom nearest to itself, producing
in this region of the helium atom a positive charge which will attract the
negative end of the water molecule. If, on the contrary, the positive end
of the water molecule happens to be nearest the helium atom, electrons
in the latter will be drawn toward the water molecule, placing a negative
charge on the part of the helium atom closest to the water molecule; the
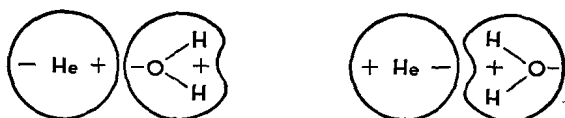opposite charges will again attract one another. The two situations may

FIG. 1.1 **Attraction between dipole of water molecule and induced dipole in a helium atom.**

be represented as in Figure 1.1. The solubility of helium in water is probably
due to this effect.

Two molecules which are near together may attract one another in yet
a different fashion, despite the fact that neither has a permanent dipole.
Because the electrons in a molecule are in constant motion, chance may
lead to a momentarily unsymmetrical charge distribution. This in turn
may affect the neighboring molecule, inducing a simultaneous and opposite
electrical dipole. Thus, two molecules such as two hydrogen molecules,
which have on an average over a period of time complete symmetry of
negative charge about the nuclei, may experience mutual attractive forces
through synchronization of electronic motions. Interactions of this sort,
usually referred to as *dispersion* forces, are responsible for the fact that
even the noble gases condense at sufficiently low temperatures.

There may thus exist, under various circumstances, attractions resulting
from the orientation of one permanent dipole by another, from the induc-
tion of a dipole by a permanent dipole, and from dispersion forces. Except
for rather highly polar molecules such as ammonia and water, the van der
Waals forces leading to condensation of gas to liquid consist largely of
dispersion forces.

Phase diagrams

Each of the forms, or states of aggregation, or structures, which a chem-
ical substance can assume is termed a *phase*. A sample of water may be

found in the vapor phase, in the liquid phase, in that solid phase commonly encountered as ice, or in one of several other solid phases which appear at high pressures and which differ from ordinary ice in the manner in which water molecules are arranged in the crystalline pattern.

More generally, a phase may be described as a homogeneous portion of a material system which, if present along with any other phases, is set off from the other phases by a boundary surface or discontinuity. A quantity of matter which is uniform in composition and structure, or homogeneous, throughout is said to consist of one phase. A one-phase system might be entirely gaseous, or might comprise a single liquid layer, or might be composed of particles of a solid all of which are of the same structural pattern or allotropic form. Another type of system is represented by liquid water with pieces of ice floating on the surface; here two phases, one liquid and one solid, are present. If benzene and water, which do not dissolve very much in one another, are mixed together, two liquid layers separated by a visible boundary surface result; again, two phases are coexisting. If liquid water is mixed with a relatively large amount of sodium chloride so that the latter does not all dissolve, the two phases present after equilibrium is reached are saturated aqueous salt solution and solid sodium chloride.

The behavior of a chemical substance under various conditions of temperature and pressure is often represented by a phase diagram. In this diagram are shown the ranges of conditions under which each of the several phases that the substance can assume may exist as a stable form, as well as the more limited conditions under which equilibrium coexistence of two or more phases is possible.

At this point we shall illustrate the interpretation of a phase diagram for a relatively simple system containing only one substance; later, more complex systems will be considered. Figure 1.2, the phase diagram for the substance water in the lower pressure region, represents schematically the results of experimental determinations of the equilibrium relations of three phases of water in the absence of air or any other foreign material, as in a closed container. In order that the distinctive features may be more clearly seen, the diagram is not drawn to scale.

Suppose that the temperature of a sample of water is 50° C. So long as the pressure remains below 92.51 mm. of mercury, the gas phase continues to be stable. If the pressure is momentarily increased to just above 92.51 mm., either by decreasing the container volume or by adding more vapor, the vapor will partially condense to liquid until the loss of gas is sufficient to restore the pressure to its equilibrium value at 50°. If the pressure is increased above 92.51 mm. and kept there by external means, the vapor will completely condense; for in these circumstances only liquid can exist. Thus there is only one pressure under which liquid and vapor of a pure substance can coexist permanently at a given temperature. Similar considerations apply to the vapor and solid: at −10° C., for example, vapor

can exist by itself at pressures below 1.95 mm. while the solid alone exists at pressures exceeding this. Only at this one particular pressure can the two phases be in equilibrium.

Water is rather unusual in that increasing pressure lowers the melting point of the solid phase; this trend is indicated by the inclination of the line o-b to the left. At about 1000 atmospheres, the solid phase and the liquid phase may be in equilibrium at $-10°$. For most substances, the solid phase is more dense than the liquid phase and tends to be formed more
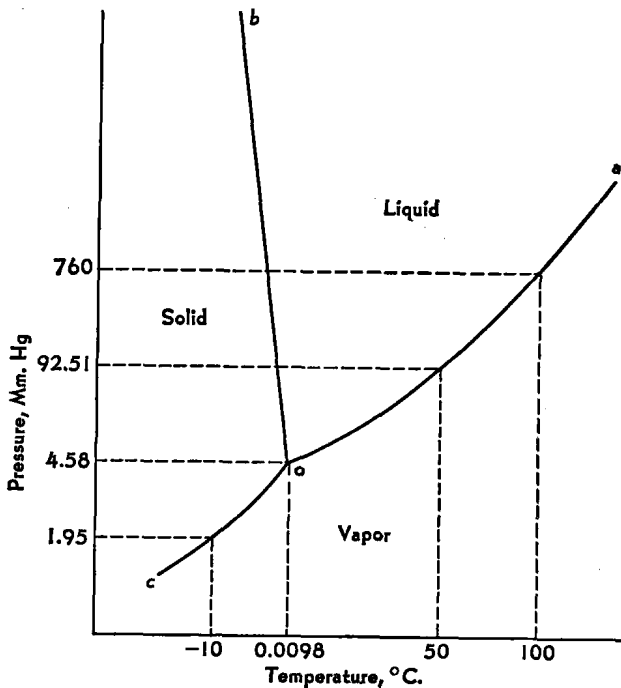

FIG. 1.2   Phase diagram of water. Other forms of ice than ordinary ice exist at high pressures beyond the range of the diagram.

readily at higher pressures, but the structure of ice is such that it is less compact and therefore less dense than liquid water at the same temperature. The phase diagram for the substance carbon dioxide is similar to that for water except for this one feature: the line corresponding to o-b and separating the solid and liquid regions slopes to the right rather than to the left.

A point of particular interest in Figure 1.2 is that designated o and known as the triple point. At this point the temperature is 0.0098° and the pressure is 4.58 mm., and it is only under these conditions that all three phases, gas, liquid, and solid, can be together in equilibrium. If the three phases

are mixed together at any other temperature or pressure, one or two of them will disappear in order to establish equilibrium. The zero of temperature on the centigrade scale is defined as the freezing point of water; this is not the same as the triple point but is the temperature at which ice and air-saturated water are in equilibrium under a total pressure of one atmosphere. Under these conditions, most of the pressure of the vapor phase is contributed by air.

1.2 GASES

The ideal gas equation

On the basis of experiment there has been evolved a generalized pattern of behavior which a number of gases closely approach and which most gases at least roughly approximate. The outstanding characteristic of a gas is the sensitivity of its volume to changes in temperature and in external pressure. An *ideal* or *perfect* gas is one for which the volume varies in direct proportion to the absolute temperature under constant pressure (Charles' Law) and in inverse proportion to the applied pressure at constant temperature (Boyle's Law):

$$V \sim T \tag{1.1}$$

$$V \sim \frac{1}{P} \tag{1.2}$$

These equations may be combined into one, useful for the prediction of volume change when both temperature and pressure vary at the same time:

$$V \sim \frac{T}{P} \tag{1.3}$$

Proportional variation implies that one quantity is equal to a constant numerical multiplier times the second quantity; thus the gas equation may be written with a constant of proportionality, c:

$$V = \frac{cT}{P} \quad \text{or} \quad PV = cT \tag{1.4}$$

A further result of experiment is the conclusion that the numerical value of the constant c varies directly with the number of gram-molecular-weights of gas in the sample being described, and is the same for samples of different gases which contain the same number of moles. If c is accordingly set equal to nR, where n is the number of moles of gas and R is called the *gas constant*, the ideal gas law becomes:

$$PV = nRT \tag{1.5}$$

This equation, it must be remembered, is a limiting equation, in the