

# **basic inorganic chemistry**

---

F. ALBERT COTTON

GEOFFREY WILKINSON

---

# basic inorganic chemistry

---

**F. ALBERT COTTON**

*Robert A. Welch Distinguished Professor of Chemistry  
Texas A and M University  
College Station, Texas, USA*

**GEOFFREY WILKINSON**

*Professor of Inorganic Chemistry  
Imperial College of Science and Technology  
University of London, England*



**JOHN WILEY & SONS, INC.**

New York London Sydney Toronto

---

## **preface**

---

*Those who aspire not to guess and divine, but to discover and know, who propose not to devise mimic and fabulous worlds of their own, but to examine and dissect the nature of this very world itself, must go to facts themselves for everything."*

F. Bacon, 1620

There are already several textbooks of inorganic chemistry that treat the subject in considerably less space than our comprehensive text, *Advanced Inorganic Chemistry*. Moreover, most of them include a great deal of introductory theory, which we omitted from our larger book because of space considerations. The net result is that these books contain very little of the real content of inorganic chemistry—namely, the actual facts about the properties and behavior of inorganic compounds.

Our purpose in *Basic Inorganic Chemistry*, is to meet the needs of teachers who present this subject to students who do not have the time or perhaps the inclination to pursue it in depth, but who may also require explicit coverage of basic topics such as the electronic structure of atoms and elementary valence theory. We therefore introduce material of this type, in an elementary fashion, and present only the main facts.

The point, however, is that this book does present the facts, in a systematic way. We have a decidedly Baconian philosophy about all chemistry, but particularly inorganic chemistry. We are convinced that inorganic chemistry *sans* facts (or nearly so), as presented in other books, is like a page of music with no instrument to play it on. One can appreciate the sound of music without knowing anything of musical theory, although of course one's appreciation is enhanced by knowing some theory. However, a book of musical theory, even if it is illustrated by audible snatches of themes and a few chord progressions, is quite unlike the hearing of a real composition in its entirety.

We believe that a student who has read a book on "inorganic chemistry" that consists almost entirely of theory and so-called principles, with but sporadic mention of the hard facts (only when they "nicely" illustrate the "principles") has not, in actual fact, had a course in inorganic chemistry. We deplore the current trend toward this way of teaching students who are not expected to specialize in the subject, and believe that even the nonspecialist ought to get a straight dose

of the subject as it really is—"warts and all." This book was written to encourage the teaching of inorganic chemistry in a Baconian manner.

At the end of each chapter, there is a study guide. Occasionally this includes a few remarks on the scope and purpose of the chapter to help the student place it in the context of the entire book. A supplementary reading list is included in all chapters. This consists of relatively recent articles in the secondary (monograph and review) literature, which will be of interest to those who wish to pursue the subject matter in more detail. In some instances there is little literature of this kind available. However, the student—and the instructor—will find more detailed treatments of all the elements and classes of compounds, as well as further references, in our *Advanced Inorganic Chemistry*, third edition, Wiley, 1972, and in *Comprehensive Inorganic Chemistry*, J. C. Bailar, Jr., H. J. Emeléus, R. S. Nyholm, and A. F. Trotman-Dickinson, eds., Pergamon, 1973.

F. ALBERT COTTON  
GEOFFREY WILKINSON

---

## contents

---

### Part 1

#### FIRST PRINCIPLES 1

1. Some Physical Chemical Preliminaries 3
2. Atomic Structure 31
3. Chemical Bonding 55
4. Ionic Solids 91
5. The Chemistry of Anions 107
6. Coordination Chemistry 125
7. Solvents, Solutions, Acids, and Bases 163
8. The Periodic Table and the Chemistry of the Elements 181

### Part 2

#### THE MAIN GROUP ELEMENTS 207

9. Hydrogen 209
10. The Group IA Elements: Lithium, Sodium, Potassium, Rubidium and Cesium 217
11. The Group IIA Elements: Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium 225
12. Boron 231
13. The Group III Elements, Aluminum, Gallium, Indium, and Thallium 247
14. Carbon 257
15. The Group IVB Elements, Silicon, Germanium, Tin and Lead 267
16. Nitrogen 275
17. The Group VB Elements, Phosphorus, Arsenic, Antimony and Bismuth 287
18. Oxygen 299
19. The Group VIB Elements, Sulfur, Selenium, Tellurium and Polonium 311
20. The Halogens, Fluorine, Chlorine, Bromine, Iodine and Astatine 321
21. The Noble Gases 337
22. Zinc, Cadmium, and Mercury 343

### Part 3

#### TRANSITION ELEMENTS 351

23. Introduction to Transition Elements. Ligand Field Theory 353
24. The First Series of *d*-Block Transition Elements 379

- 25. The Elements of the Second and Third Transition Series 419
- 26. Scandium, Yttrium, Lanthanum, and the Lanthanides 447
- 27. The Actinide Elements 457

Part 4

**SOME SPECIAL TOPICS 471**

- 28. Complexes of  $\pi$ -Acceptor ( $\pi$ -acid) Ligands 473
- 29. Organometallic Compounds 497
- 30. Organometallic Compounds in Homogeneous Catalytic Reactions 529
- 31. Metals in Biological Systems 551

**INDEX 571**

# 1

---

## First Principles

---





# 1

## some physical chemical preliminaries

### 1-1

#### Units

**1-1a** There is now an internationally accepted set of Units for the physical sciences. It is called the SI (for *Système International*) units. Based on the metric system, it is designed to achieve maximum internal consistency. However, since it requires the abandonment of many familiar units and numerical constants in favor of new ones, its adoption in practice will take time. In this book, we shall take a middle course, adopting some SI units (e.g., joules for calories) but retaining some non-SI units (e.g., angstroms).

**1-1b The SI Units.** The SI system is based on the following set of defined units:

Physical Quantity	Name of Unit	Symbol for Unit
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	kelvin	K
Luminous intensity	candela	cd

Multiples and fractions of these are specified using the following prefixes:

Multiplier	Prefix	Symbol
$10^{-1}$	deci	d
$10^{-2}$	centi	c
$10^{-3}$	milli	m
$10^{-6}$	micro	$\mu$
$10^{-9}$	nano	n
$10^{-12}$	pico	p
10	deka	da
$10^2$	hecto	h
$10^3$	kilo	k
$10^6$	mega	M
$10^9$	giga	G
$10^{12}$	tera	T

In addition to the defined units, the system includes a number of derived units, of which the following are the main ones.

Physical quantity	SI unit	Unit symbol
Force	newton	$N = \text{kg m s}^{-2}$
Work, energy, quantity of heat	joule	$J = \text{Nm}$
Power	watt	$W = \text{J s}^{-1}$
Electric charge	coulomb	$C = \text{As}$
Electric potential	volt	$V = \text{WA}^{-1}$
Electric capacitance	farad	$F = \text{As V}^{-1}$
Electric resistance	ohm	$\Omega = \text{VA}^{-1}$
Frequency	hertz	$\text{Hz} = \text{s}^{-1}$
Magnetic flux	weber	$\text{Wb} = \text{Vs}$
Magnetic flux density	tesla	$T = \text{Wb m}^{-2}$
Inductance	henry	$H = \text{Vs A}^{-1}$

### 1-1c Units To Be Used in This Book.

**Energy.** Joules and kilojoules will be used exclusively. Most of the chemical literature to date employs calories, kilocalories, electron volts and, to a limited extent, wave numbers ( $\text{cm}^{-1}$ ). See Section 1-1d for the conversion of these units to joules.

**Bond lengths.** The angstrom, Å, will be used. This is defined as  $10^{-8}$  centimeter. The nanometer ( $10^{-9}$  m) and picometer ( $10^{-12}$  m) are to be found in recent literature. The C—C bond length in diamond has the value:

1.54 angstrom

0.154 nanometers

154 picometers

**Pressure.** Atmospheres, atm, and torr ( $1/760$  atm) will be used.

### 1-1d Some Useful Conversion Factors and Numerical Constants

#### Conversion Factors:

1 calorie = 4.184 joules(j)

1 electron volt per molecule = 96.5 kilojoules per mole ( $\text{kJ mol}^{-1}$ )

1 kilojoule per mole = 83.54 wave numbers ( $\text{cm}^{-1}$ )

#### Important Constants:

Avogadro's number ( $C^{12} = 12.0000 \dots$ ),  $N_A = 6.02252 \times 10^{23} \text{ mol}^{-1}$

Electron charge,  $e = (4.8030 \pm 0.0001) \times 10^{-10}$  abs esu =  $1.602 \times 10^{-19}$  C

Electron mass,  $m = 9.1091 \times 10^{-31}$  kg = 0.00054860 mu = 0.5110 Mev

Gas constant,  $R = 1.9872$  defined cal deg $^{-1}$  mol $^{-1}$  = 8.3143 JK $^{-1}$  mol $^{-1}$  = 0.082057 liter atm deg $^{-1}$  mol $^{-1}$

Ice point:  $273.150 \pm 0.01$  K

Molar volume (ideal gas, 0°C, 1 atm) =  $22.414 \times 10^3$  cm $^3$  mol $^{-1}$  =  $2.241436 \times 10^{-2}$  m $^3$  mol $^{-1}$

Planck's constant,  $h = 6.6256 \times 10^{-27}$  erg sec  $= 6.6256 \times 10^{-34}$  Js

Boltzmann's constant,  $k = 1.3805 \times 10^{-23}$  JK $^{-1}$

Velocity of light in vacuum  $= 2.99795 \times 10^8$  msec $^{-1}$

$\pi = 3.14159$

$e = 2.7183$

$\ln 10 = 2.3026$

**1-1e Coulombic Force and Energy Calculations in SI Units.** Although SI units do, for the most part, lead to simplification, one computation that is important to inorganic chemistry becomes slightly more complex. We explain that point in detail here. It traces back to the concept of the dielectric constant,  $\epsilon$ , which relates the intensity of an electric field induced within a substance,  $D$ , to the intensity of the field applied,  $E$ , by the equation

$$D = \epsilon E$$

The same parameter appears in the Coulomb equation for the force,  $F$ , between two charges,  $q_1$  and  $q_2$ , separated by a distance,  $d$ , and immersed in a medium with a dielectric constant  $\epsilon$ :

$$F = \frac{q_1 \times q_2}{\epsilon d^2}$$

In the old (cgs) system of units, which the SI system replaces, units and magnitudes were so defined that  $\epsilon$  was a dimensionless quantity and for a vacuum we had  $\epsilon_0 = 1$ .

For reasons that we shall not pursue here, coulomb's law of electrostatic force, in SI units, must be written

$$F = \frac{q_1 \times q_2}{4\pi\epsilon d^2}$$

The charges are expressed in Coulombs, C, the distance in meters, m, and the force is obtained in newtons, N. It now develops that  $\epsilon$  has units (i.e., is no longer a dimensionless quantity), namely, C $^2$ m $^{-1}$ J $^{-1}$ . Moreover, the dielectric constant of a vacuum (the permittivity, as it should formally be called) is no longer unity. It is, instead,

$$\epsilon_0 = 8.854 \times 10^{-12} \text{C}^2 \text{m}^{-1} \text{J}^{-1}$$

Thus, to calculate a Coulomb energy,  $E$ , in joules, J, we must employ the expression

$$E = \frac{q_1 \times q_2}{4\pi\epsilon d}$$

with all quantities being as defined above for the Coulomb force.

## 1-2

## Thermochemistry

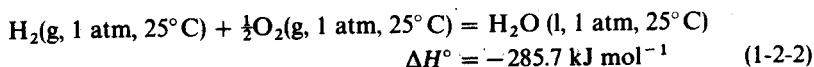
**1-2a Standard States.** To have universally recognized and understood values for energy changes in chemical processes, it is first necessary to define standard states for all substances.

The standard state for any substance is that phase in which it exists at 25°C (298.15 K) and one atmosphere (101.325 newtons per square meter) pressure. Substances in solution are at a concentration of 1 mole per liter.

**1-2b Heat Content or Enthalpy.** Virtually all physical and chemical changes either produce or consume energy, and generally this energy takes the form of heat. The gain or loss of heat may be attributed to a change in the "heat content," of the substances taking part in the process. "Heat content" is called *enthalpy*, symbolized  $H$ . The change in heat content is called the enthalpy change,  $\Delta H$ .

$$\Delta H = (H \text{ of products}) - (H \text{ of reactants}) \quad (1-2-1)$$

For the case where all products and reactants are in their standard states, the enthalpy change is represented by  $\Delta H^\circ$ , the *standard enthalpy* change of the process. For example, although the formation of water from  $H_2$  and  $O_2$  cannot actually be carried out at an appreciable rate under standard conditions, it is nevertheless useful to know, indirectly, that



The heat contents of all elements in their standard states are arbitrarily set equal to zero for thermochemical purposes.

**1-2c The Signs of  $\Delta H$ 's.** In the above equation,  $\Delta H^\circ$  has a negative value. The heat content of the products is lower than that of the reactants, which means, heat is released. In general, we have

$$\begin{aligned} \text{Heat released: } \Delta H &< 0 \\ \text{Heat absorbed: } \Delta H &> 0 \end{aligned}$$

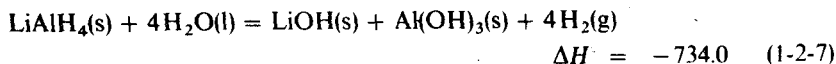
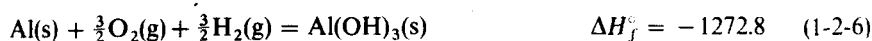
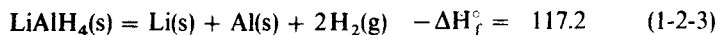
The same convention will apply to changes in free energy,  $\Delta G$ , to be discussed shortly.

Processes in which heat—or another form of energy—is released ( $\Delta H < 0$ ) are called *exothermic* or *exoergic*. Those that consume energy ( $\Delta H > 0$ ) are called *endothermic* or *endoergic*.

**1-2d Standard Heats (Enthalpies) of Formation.** The standard enthalpy change for any reaction can be calculated if the standard heat of formation,  $\Delta H_f^\circ$ , of each reactant and product is known. It is therefore useful to have tables of  $\Delta H_f^\circ$  values. The  $\Delta H_f^\circ$  value for a substance is the  $\Delta H$  value for the process in which it is

formed in its standard state from the elements, each in its standard state. Equation 1-2-2 describes such a process, and the  $\Delta H^\circ$  given is  $\Delta H_f^\circ$  of water.

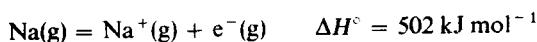
The reason  $\Delta H^\circ$  for any reaction can be calculated from  $\Delta H_f^\circ$  values is because the set of equations for the  $\Delta H_f^\circ$ 's will always add up to the equation of the desired process with the elements, other than those which may necessarily appear in the final equation, themselves canceling out. This is illustrated by Eqs. 1-2-3 to 1-2-7.



Inspection shows that all elements cancel as the Eqs. 1-2-3 to 1-2-6 are added to give 1-2-7, and it is clear that the net  $\Delta H^\circ$  is simply the sum of the  $\Delta H_f^\circ$  values of the products minus the sum of the  $\Delta H_f^\circ$  values of the reactants, each  $\Delta H_f^\circ$  being multiplied by the coefficient required by the balanced chemical equation.

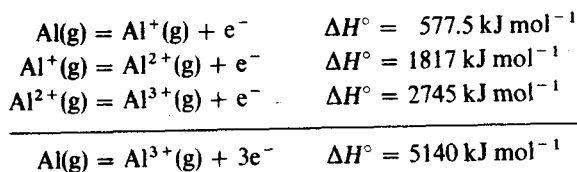
**1-2e Other Special Enthalpy Changes.** Aside from formation of a compound from the elements, there are several other physical and chemical processes of special importance for which the  $\Delta H$ , or  $\Delta H^\circ$ , values are frequently required. Among these are the processes of melting (fusion), and vaporization (of either the solid or the liquid).

**Ionization Enthalpies.** Of particular interest is the process of ionization. For example,



Thus, we speak of ionization enthalpies. Unfortunately, the more common tabulations of these quantities list them in units of the electron volt (see Section 1.1) and call them *ionization potentials*, but that terminology will not be followed here.

For many atoms, the enthalpies of removal of a second, third, etc., electron are also of chemical interest, and for most elements these enthalpies are known. For example, the first three ionization enthalpies of aluminum, and the overall energy to produce the  $\text{Al}^{3+}(\text{g})$  ion are

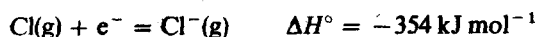


Ionization enthalpies are also defined for molecules, for example



It is to be noted that for molecules and atoms the ionization enthalpies are always positive. Energy must be supplied to detach electrons. Also, the increasing magnitudes of successive ionization steps, as shown above for aluminum, is completely general. The more positive the atom or molecule becomes, the more difficult it is to ionize it further.

*Electron Attachment Enthalpies.* Consider the following processes:



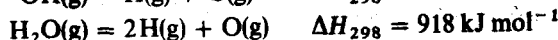
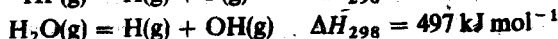
The  $\text{Cl}^-(\text{g})$  ion forms exothermically. The same is true of the other halide ions. Observe that the formation of the oxide ion,  $\text{O}^{2-}(\text{g})$  requires first an exothermic step and then an endothermic one. This is understandable because the  $\text{O}^-$  ion, which is already negative will tend to repel another electron.

In most of the chemical literature the negative of the enthalpy change,  $-\Delta H^\circ$ , for such a process is called the *electron affinity*,  $A$ , of the atom. In this book, however, we shall use only the systematic notation illustrated above.

Direct measurement of  $\Delta H_{EA}$ 's is difficult, and indirect methods tend to be inaccurate. To give an idea of their magnitudes, some of those known, with those which are mere estimates in parentheses, are listed below:

H						
-73						
Li	Be	B	C	N	O	F
-58	(+60)	(-30)	-120	(+10)	-142	-333
Na			Si	P	S	Cl
(-50)			(-135)	(-75)	-200	-348
					Se	Br
					(-160)	-324
						I
						-295

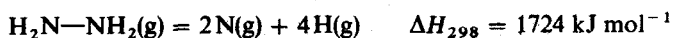
**1-2f Bond Energies.** Consider the following processes and their  $\Delta H^\circ$ 's:



The energy required in the first process has a simple, unambiguous significance. It is the energy required to break the H—F bond. It can be unambiguously called "the H—F bond energy." We can, if we prefer, think of  $566 \text{ kJ mol}^{-1}$  as the energy released when the H—F bond is formed; that is a perfectly equivalent, and equally unambiguous statement.

Consider the next three equations however. The actual processes of breaking the O—H bonds, *one after the other*, in  $\text{H}_2\text{O}$  have different energies. How then can we define “the O—H bond energy”? This requires us to refine the definition. If we take the mean of the two, which is one half of the sum,  $\frac{218}{2} = 459$   $\text{kJ mol}^{-1}$ , we can call this the *mean* O—H bond energy. This is also unambiguous, but we must remember that, knowing only this mean value, we cannot predict the actual enthalpy of either of the separate bond-breaking (or bond-forming) processes. Thus, there is a certain artificiality to the concept of the “mean” bond energy.

When we consider molecules containing more than one kind of bond the problem of defining bond energies becomes even more subtle. For example, we can think of the total enthalpy of the process



as consisting of the sum of the N—N bond energy,  $E_{\text{N—N}}$ , and four times the N—H bond energy,  $E_{\text{N—H}}$ . But is there any unique or rigorous way to divide the total energy into these component parts? The answer is no. The practical approach used is as follows.

We know from experiment that



and thus we can say that

$$E_{\text{N—H}} = \frac{1172}{3} = 391 \text{ kJ mol}^{-1}$$

If we make the *assumption* that this value can be transferred to  $\text{H}_2\text{NNH}_2$ , then we can evaluate the N—N bond energy:

$$\begin{aligned} E_{\text{N—N}} + 4E_{\text{N—H}} &= 1724 \text{ kJ mol}^{-1} \\ E_{\text{N—N}} &= 1724 - 4E_{\text{N—H}} \\ &= 1724 - 4(391) \\ &= 160 \text{ kJ mol}^{-1} \end{aligned}$$

By proceeding in this way it is possible to build up a table of bond energies from which the enthalpies of forming molecules from their constituent gaseous atoms can be calculated fairly accurately in many cases. That this is possible shows the important fact that the energy of the bond between a given pair of atoms is fairly independent of the molecular environment in which that bond occurs. This is only approximately true, but it is a good enough approximation to be useful in understanding and interpreting many chemical processes.

Thus far only single bonds have been discussed. Certain pairs of atoms, for example, C with C, N with N, C with N, C with O, can form single bonds, double bonds, and even triple bonds. The bond energy increases as the bond order increases, in all cases. However, the increase is not, in general, linear. *Figure 1-1* gives some representative data.

A list of some useful bond energies is presented in Table 1-1.

Table 1-1 Some Average Thermochemical Bond Energies at 25° in kJ mol<sup>-1</sup>

Table 1-1 Some average measurements

A. Single bond energies														
	H	C	Si	Ge	N	P	As	O	S	Se	F	Cl	Br	I
H	436	416	323*	289	391	322	247	467	347	276	566	431	366	299
C		356	301	255	285	264	201	336	272	243	485	327	285	213
Si			226	—	335	—	—	368	226	—	582	391	310	234
Ge				188	256	—	—	—	—	—	—	342	276	213
N					160	~200	—	201	—	—	272	193	—	—
P						209	—	~340	—	—	490	319	264	184
As							180	331	—	—	464	317	243	180
O								146	—	—	190	205	—	201
S									226	—	326	255	213	—
Se										172	285	243	—	—
F											158	255	238	—
Cl												242	217	209
Br													193	180
I														151

B. Multiple bond energies							
C=C	598	C≡N	616	C=O	695	N=N	418
C≡C	813	C≡N	866	C≡O	1073	N≡N	946



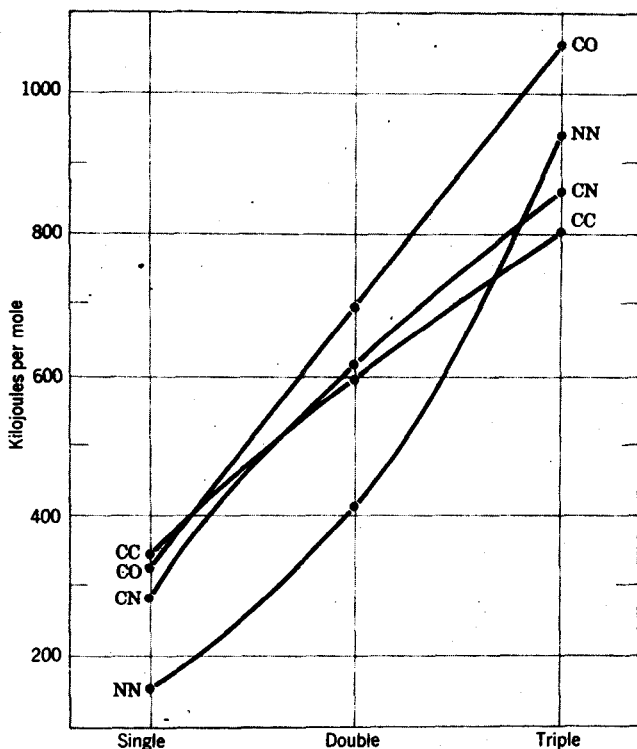


Figure 1-1 The variation of bond energy with bond order for CC, NN, CN and CO bonds.

### 1-3

#### Free Energy and Entropy

The direction in which a chemical reaction will go, or the point at which equilibrium will be reached depend on two factors: (1) The tendency to give off energy; exothermic processes are favored. (2) The tendency to attain a state that is statistically more probable, crudely describable as a "more disordered" state.

We already have a measure of the energy change of a system, namely, the magnitude and sign of  $\Delta H$ .

The statistical probability of a given state of a system is measured by its *entropy*, denoted  $S$ . The greater the value of  $S$ , the more probable (and, generally, more disordered) is the state. Thus we can rephrase the two statements made in the first paragraph as follows. The likelihood of a process occurring increases as (1)  $\Delta H$  becomes more negative, or (2)  $\Delta S$  becomes more positive.

Only in rare cases, an example being racemization,



does a reaction have  $\Delta H = 0$ . In such a case, the direction and extent of reaction depends solely on  $\Delta S$ . In the case where  $\Delta S = 0$ ,  $\Delta H$  would alone determine the