Some thermodynamic aspects of inorganic chemistry

D.A.JOHNSON

Second edition

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SECOND EDITION

CAMBRIDGE UNIVERSITY PRESS
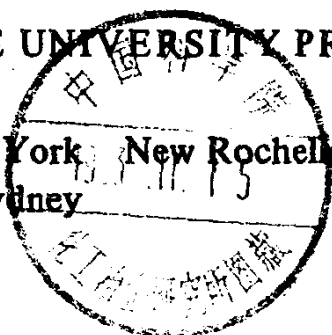Cambridge
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PREFACE TO THE SECOND EDITION

This edition has SI units. Chapter 6 has been largely rewritten, and substantial changes have been made to chapter 7. The remainder of the main text has not been greatly altered, but a lot of new material has been included by introducing problems which are at the end of each chapter. Some of these problems simply provide practice in routine operations discussed in the main text; others extend the ideas introduced in the chapters, occasionally in an argument which is sustained over several problems. Some of the questions are injudiciously speculative but, in spite of this, I have tried to provide answers and comments for each one. The answers follow the problems. Where they are numerical, they are often, for didactic reasons, given with a precision which the approximations do not warrant.

Since the first edition was published, I have continued to enjoy the friendship and inspiration of Peter Nelson. Some of the ideas in chapter 6 are the fruits of an easy, but prolonged collaboration, and it would now be impossible to disentangle our individual contributions. However, as I have not always been sensible enough to take Peter's advice, I must accept responsibility for this particular version. I should also like to thank Professor John Corbett for some helpful criticisms of the first edition, Dr Elaine Moore for advice on one or two theoretical points, and Mrs Mary Golden for her patient typing.

Finally, I am grateful to my colleagues in the Chemistry Department at the Open University, especially the permanent inmates of the temporary annexe; their companionship has made an institution which is not devoid of stress, a pleasure to work in.

Open University, Milton Keynes
24 April 1981

FROM THE PREFACE TO THE FIRST EDITION

This book is designed as a supplement to the more comprehensive works that are used by students taking a university course in inorganic chemistry. I have assumed that readers are acquainted with the elementary thermodynamics of chemical equilibria.

There are a number of people whose help I should like to acknowledge. By their disinterested award of a research fellowship, the Master and Fellows of Trinity Hall, Cambridge, furnished me with the independence that I needed to write the book. I should like to thank them for the individual kindnesses that they showed me and, with the exception of one or two convivial historians, for concealing any dismay at my dilatory progress.

Professor E. A. V. Ebsworth provided me with a great deal of patient encouragement while Dr D. A. Haydon, Dr D. J. Miller, Dr A. G. Robiette and Dr R. Walsh all suggested valuable alterations to certain sections of the text. Both Dr A. G. Sharpe, who by some stimulating undergraduate and graduate supervision first introduced me to the subject of this book, and Dr J. J. Turner, read the greater part of the manuscript at different stages and made a number of very helpful criticisms.

During the preparation of successive drafts, much my most generous helper was Dr P. G. Nelson, Lecturer in Inorganic Chemistry at the University of Hull. The treatment of d^n ionization potentials by separation of the coulombic and exchange terms is taken from his Ph.D. thesis, and it was he who suggested to me the idea of differentiating functions of the simple Kapustinskii equation. He made many other very valuable contributions in the absorbing hours of discussion that were spent while I enjoyed his hospitality at Hull. As these are too numerous to mention, perhaps the best thing I can do is to express my admiration of his mastery of chemical exposition and of his profound understanding of the subject.

None of the friends and colleagues that I have mentioned is to blame for the errors or imperfections in the book. For these I take full responsibility.

Ames, Iowa
15 March 1968

CONTENTS

1 Introduction

1.1 Stability

Inorganic chemistry tries, among other things, to account for the differing stabilities of different chemical systems. A system is said to be stable if it does not appear to change with time. Physical chemistry draws a sharp distinction between real and apparent stability. In the first case the system is in a state of equilibrium, and is stable in the strict sense of the word: that is, none of the conceivable changes in the system can occur spontaneously. In the second case the system is not in a state of equilibrium and is only apparently stable: that is, at least one of the conceivable changes can occur spontaneously but it does so at an immeasurably slow rate. The first type of stability is studied by that branch of physical chemistry known as thermodynamics; the second by that called reaction kinetics.

1.2 Thermodynamic stability[1]

For any chemical reaction,

$$aA + bB + cC + \ldots \rightarrow kK + lL + mM + \ldots \qquad [1.1]$$

the position of equilibrium is conveniently expressed in terms of the equilibrium constant K, a function of the activities, a, of the reactants and products:

$$K = \frac{a_K^k \cdot a_L^l \cdot a_M^m \cdot \ldots}{a_A^a \cdot a_B^b \cdot a_C^c \cdot \ldots} \qquad (1.1)$$

For pure liquids and solids at normal pressures, it is a very good approximation to put the activity equal to one. For solution components, whether the continuous phase be solid, liquid or gas, the activity can usually be replaced without severe error by the concentration, if the solutions are fairly dilute.

For the application of thermodynamics to descriptive chemistry, an equation relating equilibrium constants to chemical energy is essential. This is

[1] Thermodynamic properties in this book are quoted at 298.15 K unless otherwise stated. Values of fundamental constants are taken from *Quantities, Units and Symbols*, 2nd edition, Royal Society, 1975.

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provided by the van't Hoff isotherm

$$-\Delta G_m^\ominus = RT \ln K \qquad (1.2)^2$$

$\Delta G_m^\ominus$ is the standard free energy or Gibbs energy change of the reaction to which K refers. In tables of thermodynamic data, it is the standard free energy of formation of a compound, $\Delta G_f^\ominus$, that is usually recorded. For any balanced reaction, at constant temperature,

$$\Delta G_m^\ominus = \Sigma \Delta G_f^\ominus \text{ (products)} - \Sigma \Delta G_f^\ominus \text{ (reactants)} \qquad (1.3)$$

so standard free energies of reactions may readily be computed from the tables. Converting to logarithms to the base ten at 298.15 K, and expressing energies in kJ mol⁻¹, (1.2) becomes

$$-\Delta G_m^\ominus / \text{kJ mol}^{-1} = 5.708 \log K \qquad (1.4)$$

A large positive value of $\Delta G_m^\ominus$ for any reaction implies a very small equilibrium constant. The reactants are then thermodynamically stable with respect to the formation of the products, because only very small amounts of the latter need be formed to reach equilibrium. Conversely, a large negative value of $\Delta G_m^\ominus$ implies a big equilibrium constant and instability of the reactants, because the formation of considerable quantities of products is necessary before equilibrium is achieved.

$\Delta G_m^\ominus$ is dependent only upon the initial and final states in a chemical equation. Thus thermodynamic stability or instability is independent of the path or mechanism of the reaction. The same cannot be said for kinetic stability. A chemical species is kinetically stable when it possesses one or more possible modes of decomposition that are thermodynamically favourable, but which proceed at immeasurably slow rates.

1.3   Kinetic stability

The rate equation for a chemical process,

$$a\text{A} + b\text{B} + c\text{C} + \ldots \rightarrow \text{products} \qquad [1.2]$$

usually takes the form

$$\text{rate} = k[\text{A}]^{n_a}[\text{B}]^{n_b}[\text{C}]^{n_c} \ldots \qquad (1.5)$$

where n_a is the order of the reaction with respect to the reagent A, and k is the velocity constant. In more complex systems the rate may be expressed as the sum of such terms. Experimentally, the variation of the velocity constant with temperature may usually be represented, to a good approximation, by the Arrhenius equation:

$$k = A \exp(-E/RT) \qquad (1.6)$$

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² For a comment on the relation between K of (1.1) and K of (1.2), see appendix 1.

where A and E are positive quantities that change very little with temperature. As

$$\ln k = \ln A - E/RT \tag{1.7}$$

a plot of $\ln k$ against $1/T$ gives a line of slope $-E/R$, from which E and A may be determined. Between them, (1.5) and (1.7) imply that the rate of chemical reaction is increased by heating. Denoting the parameters for the forward and backward reaction by the subscripts f and b respectively, (1.6) gives

$$k_f/k_b = A_f/A_b \exp\left[-(E_f - E_b)/RT\right] \tag{1.8}$$

As

$$K = k_f/k_b \tag{1.9}$$

and, from (1.2),

$$K = \exp\left(-\Delta G_m^\ominus/RT\right) \tag{1.10}$$

$$= \exp\left(+\Delta S_m^\ominus/R\right) \cdot \exp\left(-\Delta H_m^\ominus/RT\right) \tag{1.11}$$

identification of the terms in (1.8) with those in (1.11) yields

$$\Delta H_m^\ominus = E_f - E_b \tag{1.12}$$

and

$$A_f/A_b = \exp\left(+\Delta S_m^\ominus/R\right) \tag{1.13}$$

These results suggest that the constant E should be interpreted as an enthalpy term. A way of doing this may be demonstrated by using the very simple process

$$A + BC \rightarrow AB + C \tag{1.3}$$

as an example. A possible reaction mechanism involves the close approach of A to the molecule BC followed by expulsion of C with the rupture of the B—C bond. During this process, the energy of the system will increase from that of (A + BC), reach a maximum with the formation of some configuration such as (A...B...C), and finally decline to that of (AB + C) with the elimination of C. E may be equated to the enthalpy difference between (A...B...C), which is called the activated complex, and (A + BC). It is then known as the activation energy. These changes are illustrated by the profile *RQP* in figure 1.1. The reaction coordinate, which is plotted along the *x* axis, is some parameter that represents the changes in molecular geometry that occur in the course of the reaction. The probability of the reactants having an energy sufficient for the formation of the activated complex will be low when the activation energy is high, and, for given concentrations, the process will then be much slower. These facts are in qualitative agreement with (1.5) and (1.6).[3]

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[3] A more detailed treatment of the matters discussed in this section may be found in standard texts on reaction kinetics, e.g. Laidler (1966).

The course of a reaction may be more complicated than it is for this process. It may, for example, consist of a series of elementary steps like *RQP*, and the energy profile will then show distinct minima which may correspond to intermediates of an appreciable lifetime. In this case, the energy of the highest transition state will determine the rate of the reaction.

The mechanism of a reaction is altered by the addition of a catalyst but the thermodynamics remain unchanged. In figure 1.1, the catalyst might, for example, enable an intermediate *T* to be formed. If the equilibrium between *T* and the reactants was very rapidly established, the rate-determining step would be the conversion of *T* to the products. This type of behaviour is common, but is only indirectly related to the accelerating role of the catalyst. The energy difference between the upper transition state, *S*, and the reactants is still the observed activation energy, and if this is less than *E*, then in the absence of a very unfavourable change in the pre-exponential factor, *A*, the catalysed reaction is faster. However, because the catalyst is unchanged when the reaction is over, the initial and final states remain the same. Thus the equilibrium is unperturbed.

1.4   The interpretation of stability

The single phenomenon of catalysis pinpoints a distinct difference between the sciences of kinetics and thermodynamics. In figure 1.1, the speed of the reaction is much affected by the difference in the energy ordinates of

Figure 1.1. Possible paths for a chemical reaction in the absence (*RQP*) and presence (*RTSP*) of a catalyst.
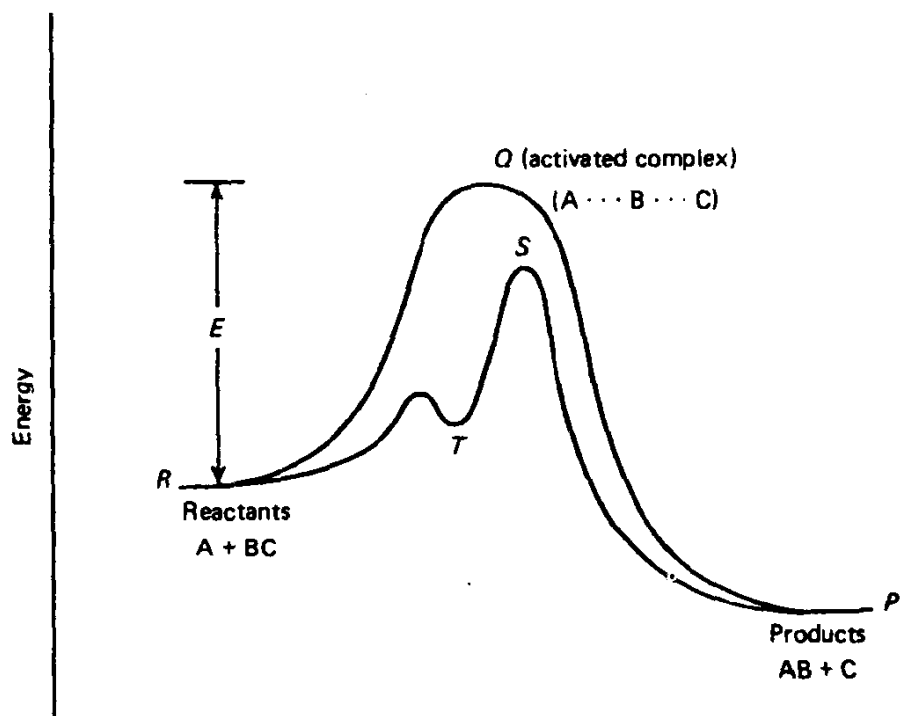
points R and Q, while the position of equilibrium depends upon that of points R and P. Thus there can be no general connection between the rate of a reaction and its equilibrium constant, and no connection in specific cases unless a relation is established between the energy of reaction and the energy of activation. This point is rather difficult to accept, because there is undoubtedly some kind of overall inverse correlation between reaction velocity and standard free energy change. Indeed in some cases, such as the oxygen or hydrogen over-voltages that are required for the rapid decomposition of water, this correlation has become something of an empirical principle although exceptions are well known (see §4.11). Nevertheless, immeasurably slow but very favourable reactions, like the combustion of methane at room temperature

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l);$$

$$\Delta G_m^{\ominus} = -818 \text{ kJ mol}^{-1} \qquad [1.4]$$
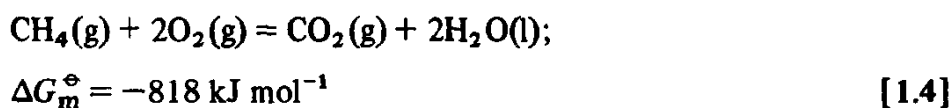
when contrasted with the speed of processes which have almost zero free energy change

$$Fe(H_2O)_6^{2+}(aq) + D_2O(l) = Fe(H_2O)_5(HDO)^{2+}(aq) + HDO(l) \qquad [1.5]$$
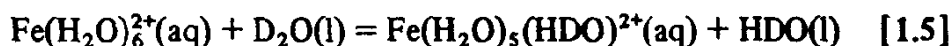
enforce general acquiescence in the more pessimistic view. Consequently a compound may be stable either for kinetic or for thermodynamic reasons, and no conclusion as to the one may be drawn from the other. If, therefore, an explanation is advanced for the stability of a compound, it is essential to decide whether this explanation applies to the rate or to the equilibrium constant of the reaction, for until this analysis has been made the interpretation cannot be complete.

The distinction between thermodynamic and kinetic stability should always be remembered. Neither the theory of the kinetics, nor of the thermodynamics, of reactions could be said to be at an advanced stage; but because a single reaction may proceed by a number of mechanisms, and because their short lifetimes make the characterization and investigation of transition states very difficult, the theory of kinetics is less well understood. This book is almost entirely concerned with thermodynamic stability.

It is an instructive exercise to examine the limitations that this approach imposes upon an assessment of the stability of a compound. In pursuing this question, the standard free energy of formation of the compound would first have to be obtained, either by calculation or by experimental measurement. From the standard free energies of formation of all possible decomposition products, the standard free energies of all decomposition reactions could then be determined. If all these values of $\Delta G_m^{\ominus}$ were positive, the compound would be stable. If one or more were negative, it might be stable or it might not, for a thermodynamically favourable reaction could be

inhibited for kinetic reasons. Clearly the interpretation of chemical stability or instability is a very formidable task, and, by itself, the science of thermodynamics can yield only a partial solution. Nevertheless, viewed comprehensively, the thermodynamic approach to the problem of stability is more important than the kinetic, because reactions with substantially positive values of $\Delta G_m^{\ominus}$ simply cannot occur. About this important class of reactions, reaction kinetics, by its very nature, can have nothing useful to say.

When discussing the instability of a compound, it is essential to consider the reaction to which it is unstable. This apparently obvious point is sometimes ignored. For example, an interpretation of the negative standard free energy of formation of a compound is sometimes cited as an explanation of its stability. There is, however, little doubt that the compounds $ScCl_2$ and $MnCl_3$, which are unknown at 298.15 K, have very negative values of $\Delta G_f^{\ominus}$, but their instability is related to the decomposition reactions

$$3ScCl_2(s) = Sc(s) + 2ScCl_3(s) \qquad\qquad [1.6]$$

$$MnCl_3(s) = MnCl_2(s) + \tfrac{1}{2}Cl_2(g) \qquad\qquad [1.7]$$

which have negative standard free energies at this temperature. Again, theoretical chemistry is much concerned with the stabilities of compounds with respect to their constituent atoms; these stabilities in nearly all cases are only indirectly related to real thermodynamic stability. Where the word 'stability' is used or implied in this book, an attempt has been made to relate it to a particular reaction or decomposition.

One more difficulty in the interpretation of stability should be mentioned. (1.4) shows that, at 298.15 K, a factor of ten in the equilibrium constant is equivalent to only 5.71 kJ mol^{-1}. Its logarithmic dependence means that a calculated equilibrium constant is very sensitive to small errors in $\Delta G_m^{\ominus}$. As any kind of theoretical approach to the estimation of equilibrium constants is usually based on the calculation of energies, (1.4) quite plainly implies that the interpretation of stabilities is a very formidable problem.

1.5 Enthalpy and entropy terms

When considering the free energies of reactions, it is often convenient to split them into two parts. For any isothermal process

$$\Delta G = \Delta H - T\Delta S \qquad\qquad (1.14)$$

where ΔS is the entropy change and ΔH is the enthalpy change, which is related to q_p (the heat absorbed at constant pressure) by the equation

$$\Delta H = q_p \qquad\qquad (1.15)$$

The standard enthalpy change of a reaction occurring at constant temperature may be calculated if the standard enthalpies of formation of the

Table 1.1. *Standard molar entropies at* 298.15 K

Substance	$S^{\ominus}$/J K^{-1} mol^{-1}	Substance	$S^{\ominus}$/J K^{-1} mol^{-1}
$H_2(g)$	130.6	$NF_3(g)$	260.6
$F_2(g)$	202.7	$BF_3(g)$	254.0
$Br_2(l)$	152.2	$BCl_3(g)$	290.0
$Br_2(g)$	245.4	$BBr_3(g)$	324.1
$I_2(s)$	116.1	$ClO_2(g)$	256.7
$I_2(g)$	260.6	$SO_2(g)$	248.1
C (graphite)	5.7	$NO_2(g)$	240.0
C(g)	158.0	$N_2O_4(g)$	304.2
HCl(g)	186.8	$OsO_4(s)$	143.9
$NH_3(g)$	192.3	$OsO_4(g)$	293.7
$NH_4Cl(s)$	94.6	$MoF_6(g)$	350.4
$H_2O(g)$	188.7	$Al_2Cl_6(g)$	490
$H_2O(l)$	69.9	$TiCl_4(l)$	252.3
		$TiCl_4(g)$	354.8

reactants and products are known, for then

$$\Delta H_m^{\ominus} = \Sigma \Delta H_f^{\ominus} \text{ (products)} - \Sigma \Delta H_f^{\ominus} \text{ (reactants)} \qquad (1.16)$$

Because the standard molar entropies of elements or compounds may be determined by using the third law of thermodynamics, it is these, rather than the standard entropies of formation, that are recorded in most compilations. For any reaction,

$$\Delta S_m^{\ominus} = \Sigma S^{\ominus} \text{ (products)} - \Sigma S^{\ominus} \text{ (reactants)} \qquad (1.17)$$

The melting of a solid or the boiling of a liquid occurs reversibly at the transition temperature. Thus

$$dS = q/T \qquad (1.18)$$

and

$$\Delta S_{tr}^{\ominus}(T) = \Delta H_{tr}^{\ominus}(T)/T \qquad (1.19)$$

where $\Delta H_{tr}^{\ominus}(T)$ is the standard enthalpy of the phase transition at temperature T, T in this case being the melting or boiling temperature at 1 atm. As standard enthalpies of evaporation usually exceed those of fusion by a substantial amount, $\Delta S_{tr}^{\ominus}(T)$ for an evaporation is particularly large. This means that the entropies of gases are, in general, considerably greater than those of liquids, which, in turn, are greater than those of solids. Some sample figures are presented in table 1.1.

1.6 The entropies of gases

The entropy of a gas depends on the number of different energy levels over which its molecules are spread. The larger this number the larger is

Table 1.2. *Analysis of the standard molar entropies of some gases*

	$C_6H_6(g)$	$CH_4(g)$	$CCl_4(g)$	$CH_3CCl_3(g)$
$S^{\ominus}_{trans}/J\ K^{-1}\ mol^{-1}$	163.1	143.4	171.5	169.8
$S^{\ominus}_{rot}/J\ K^{-1}\ mol^{-1}$	86.8	42.4	98.8	119.0^a
$S^{\ominus}_{vib}/J\ K^{-1}\ mol^{-1}$	19.3	0.4	39.6	34.2
$S^{\ominus}_{elect}/J\ K^{-1}\ mol^{-1}$	–	–	–	–
$S^{\ominus}_{total}/J\ K^{-1}\ mol^{-1}$	269.2	186.2	309.9	323.0

^{a} Includes a 9.2 J K^{-1} mol^{-1} contribution from internal rotation.

the number of ways in which the individual molecules can be assigned to the energy levels. This necessarily implies that the molar entropy is greater. For a discussion see Denbigh (1971). In most of the cases with which we shall be concerned, the gas molecules will be in an electronic ground state which contains no unpaired electrons, and the population of excited electronic states will be negligible. Under these circumstances, the energy levels occupied by the gas molecules can be classified under three kinds of motion: translational, rotational and vibrational; and each of these makes its contribution to the entropy of the gas. Some examples of this breakdown of the standard molar entropy are given in table 1.2.

Statistical mechanics shows that the separations of the quantized energy levels for translational motion diminish with particle mass. At any temperature, therefore, more energy levels will be occupied in gases of higher molecular mass, and the translational contribution to the molar entropy will be correspondingly larger. This is particularly noticeable in the case of monatomic gases. Provided our neglect of the electronic contribution is justified, the translational contribution then comprises the whole of the entropy and is given by the Sackur-Tetrode equation:

$$S = nR \ln \{e^{5/2}(2\pi mkT/h^2)^{3/2}(kT/p)\} \tag{1.20}$$

where n is the number of moles, m is the mass of one molecule, and k and h are Boltzmann's and Planck's constants respectively. For a gas in its standard (ideal gas) state at 1 atm and 298.15 K, this reduces to

$$S^{\ominus} = \tfrac{3}{2}R \ln M_r + 108.745\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{1.21}$$

where M_r is the molar mass. When the gas is not monatomic, this equation gives just the translational contribution. Thus, for benzene $M_r = 78.11$, and the substitution in equation (1.21) gives $S^{\ominus}_{trans} = 163.10$ J K^{-1} mol^{-1} in agreement with table 1.2.

In the case of rotational motion, the separation of the energy levels diminishes as the moments of inertia about the three perpendicular axes of

the molecule increase. To illustrate this we can compare CH_4 with CCl_4 in table 1.2. Not only are the four peripheral atoms more massive in the chloride, but they are displaced from the centre of gravity of the molecule by a larger bond length. Thus, at a given temperature, more rotational levels are occupied in CCl_4 than in CH_4, and $S^{\ominus}_{rot}$ is correspondingly larger.

Two other contributions to the rotational entropy are worth mentioning. First, in more symmetrical molecules, certain rotational energy levels are excluded by the symmetry of the wave function (Mayer and Mayer, 1940), so the rotational entropy is less than it would otherwise be. This lowering is given by $R \ln \sigma$ where σ, the *symmetry number*, is equal to the number of indistinguishable orientations that the molecule can occupy in space. For example, if we label one of the hydrogen atoms in methane H(1), and look down the C—H(1) bond, we see that there are three indistinguishable positions corresponding to three successive 120° rotations about the C_3 axes. We could then successively bring H(2), H(3) and H(4) to the H(1) position and repeat the operations, each time generating a further three indistinguishable positions. This gives 4×3 indistinguishable positions in all, so $\sigma = 12$. Were it not for the $R \ln \sigma$ term, therefore, $S^{\ominus}_{rot}(CH_4,g)$ would be $20.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$ greater than the correct value in table 1.2.

So far we have considered just those rotational levels provided by the overall rotation of the molecule. The second additional contribution to the rotational entropy which is of interest occurs in more complex molecules containing groups which undergo either free or restricted *internal rotation* within the molecule itself. This motion generates energy levels which also make their contribution to the entropy. Thus, in the case of 1,1,1-trichloroethane, there is restricted rotation of the CH_3 and CCl_3 groups with respect to one another; as table 1.2 reveals, this contributes about 3% of the molar entropy at 298.15 K.

In general, the separations of the energy levels generated by the vibrational motion of a molecule are some 100 times greater than those of the rotational levels. At 298.15 K, therefore, population of excited vibrational states is usually small, and the same can be said of the vibrational entropy. However, the separation of the energy levels increases with vibrational frequency, and as vibrational frequencies are usually larger when the vibrating atoms have low masses, the vibrational contribution to the entropy will be larger in molecules containing heavier atoms. Compare, for example, CH_4 and CCl_4 in table 1.2. The vibrational contribution will also tend to increase with molecular complexity as the number of vibrational modes increases.

Finally, although we have chosen to ignore entropy contributions due to the presence of excited electronic states, we should mention one kind of electronic entropy which is possessed by molecules with a degenerate electronic ground state. For example, the molecule NO_2 contains an unpaired electron and has a $^2A_1$ ground state. The spin angular momentum can take