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THE CALCULATION OF FREE ENERGY FROM SPECTROSCOPIC DATA

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For many years it has been evident that the utilization of the observed energy levels of atoms and molecules was destined to occupy a prominent place in the application of thermodynamics and statistics to chemistry. However, it is doubtful whether the very real simplicity of this application has been appreciated as it should be. Perhaps this is not surprising when one considers the unnecessarily complicated methods often used in treating such problems. It is the purpose of this paper to give the few simple statements necessary in connection with the exact determination of certain thermodynamic properties from the energy levels of matter as supplied by spectroscopy.

At the present time it is possible to make accurate calculations only for the perfect gaseous state. Interpreted spectroscopic data are available only for relatively simple molecules.

For the usual purposes of chemistry it is convenient to consider a large group of molecules as a single state without investigating the intimate details of their individual existences. However, in order to make a precise statistical calculation of a thermodynamic property, one must have an itemized account of all the states among which the molecules are distributed in appreciable concentrations. It may be well to add that the state of a molecule has a perfectly definite meaning only to the extent to which it is not appreciably influenced by neighboring molecules.

Let us be clear as to the meaning of a state. Every state corresponds to certain definite quantum specifications which are not possessed in every particular by any other state. Fortunately spectroscopy supplies the necessary information about atomic and molecular states and often more accurately than is necessary for ordinary purposes.

Every state is assumed to have equal statistical weight. This means that given equal opportunity to possess the energies necessary for their separate existences, all states are equally probable. The convenient use of *a priori* probability to include a group of states has caused some ambiguity in the use of the term state. A statement to the effect that a certain "state" has an *a priori* weight of three, means that the "state" is really three states which have been grouped together for simplicity of calculation. This is customary when the states have so nearly the same energies that they are affected in nearly the same way by temperature. However, it should be remembered that they are individual states in a statistical sense.

The problem of finding the distribution of atoms and molecules among

the various possible states existing in a gas may, for convenience, be divided into two parts, namely, the problem of translation, and that dealing with all other possible energy absorption. The quantum-statistical treatment of the properties of an ideal gas was first given by Sackur¹ and by Tetrode.² Later Stern³ and Ehrenfest and Trkal⁴ contributed much clearer treatments. The logic of these earlier treatments left much to be desired, but this difficulty has recently been removed by the introduction of Bose-Einstein statistics. A very satisfactory treatment of this subject, with references to the previous work, has been given by Lewis and Mayer.⁵ The final results for the properties of an *ideal* gas possessing translation alone are always the same for the various treatments which have been given. We have nothing to add to this subject but recall attention to the fact that the translational properties of all molecules, however complicated, are represented by the same equations when they are in the ideal gas state. This will be used as a starting point. The equations for the entropy of translation will be quoted later.

The thermodynamic properties of gases are usually referred to the standard state, which is the ideal gas state, and this may be treated simply and accurately when the necessary energy levels are available. The corrections to the actual gas at moderate pressures may usually be neglected at ordinary temperatures or above, but in any case are readily obtained from the data of state. The determination of the distribution of atoms and molecules among the various possible states may be approached by means of thermodynamics or by statistics. The usual thermodynamic method considers the equilibrium between any two states

$$B = B' \quad \Delta F^\circ = -RT \ln \frac{n'}{n}$$

There is no entropy change in such a transition since each of the states has unit *a priori* statistical weight. Thus for this simple process the free energy change $\Delta F = \Delta E$, the energy change, when the particles are taken to be a perfect gas. Then the ratio of the numbers in the two states

$$\frac{n'}{n} = e^{-\Delta E/RT} = e^{-(\epsilon' - \epsilon)/kT} \quad \text{the Boltzmann factor}$$

$\epsilon' - \epsilon$ and k refer to the energy difference and the gas constant per molecule, respectively.

Derivations of the Boltzmann factor from statistics may be found in numerous books dealing with statistical mechanics. A simple derivation has been given by Lewis and Mayer.⁵ In agreement with Einstein they show that the Boltzmann factor is not quite correct, due to quantum

¹ Sackur, *Ann. Physik*, **36**, 968 (1911).

² Tetrode, *ibid.*, **38**, 434 (1912).

³ Stern, *Physik. Z.*, **14**, 629 (1913); *Z. Electrochem.*, **25**, 66 (1919).

⁴ Ehrenfest and Trkal, *Proc. Akad. Sci. Amsterdam*, **23**, 162 (1920).

⁵ Lewis and Mayer, *Proc. Nat. Acad. Sci.*, **15**, 208 (1929).

degeneracy, but since our discussion will deal only with the standard state which is non-degenerate by definition, we may accept the Boltzmann factor as exactly true.

With the assistance of the Boltzmann factor one may readily obtain the desired thermodynamic properties. Let N be Avogadro's number and A the number of molecules in the lowest energy, or zero state (excluding translation). Then as usual the number in the first state is equal to $Ae^{-\epsilon_1/kT}$, where ϵ_1 is the observed energy per molecule with reference to the zero state. The number in the r^{th} state will be $Ae^{-\epsilon_r/kT}$. From this it follows that

$$N = p_0A + p_1Ae^{-\epsilon_1/kT} + p_2Ae^{-\epsilon_2/kT} + \dots \quad (1)$$

where the p 's are the *a priori* probabilities referred to above and it may be well to repeat for emphasis that each term in the above expression is actually p separate terms with so nearly the same Boltzmann factors that the difference may be neglected. The total energy above the zero point of the system (excluding translation) is given by the expression

$$E^\circ - E_0^\circ = p_0A + \epsilon_1 p_1 A e^{-\epsilon_1/kT} + \epsilon_2 p_2 A e^{-\epsilon_2/kT} + \dots \quad (2)$$

where E_0° is the energy of the substance in the perfect gas state at the absolute zero of temperature. The superscript $^\circ$ is used to designate a property of the substance in its standard reference state, in this case the hypothetical ideal gas state with a pressure of one atmosphere. This follows the conventions of Lewis and Randall,⁶ which will be used where possible. Eliminating A from Equations 1 and 2, and making use of the abbreviation afforded by the summation sign

$$E^\circ - E_0^\circ = N \frac{\sum \epsilon p e^{-\epsilon/kT}}{\sum p e^{-\epsilon/kT}} \quad (3)$$

$$= RT^2 \frac{d \ln Q}{dT}, \text{ where} \quad (4)$$

$$Q = p_0 + p_1 e^{-\epsilon_1/kT} + p_2 e^{-\epsilon_2/kT} + \dots \quad (5)$$

These series contain terms for every state that the molecule can assume.

Differentiation of $E^\circ - E_0^\circ$ with respect to T gives the heat capacity due to the degrees of freedom considered, thus

$$\frac{dE^\circ}{dT} = \frac{N}{kT^2} \left[\frac{\sum \epsilon^2 p e^{-\epsilon/kT}}{\sum p e^{-\epsilon/kT}} - \left(\frac{\sum \epsilon p e^{-\epsilon/kT}}{\sum p e^{-\epsilon/kT}} \right)^2 \right] \quad (6)$$

$$= -R \frac{d}{dT} \frac{d \ln Q}{d 1/T} \quad (7)$$

a well-known equation which was first applied to the actual energy levels of a molecule by Hicks and Mitchell,⁸ who, at the suggestion of Tolman, calculated the rotational-vibrational heat capacity of hydrogen

⁶ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

⁷ Reiche, *Ann. Physik*, **58**, 657 (1919).

⁸ Hicks and Mitchell, *THIS JOURNAL*, **48**, 1520 (1926).

chloride. Their results are unfortunately marred by an error in connection with the *a priori* probabilities.⁹

Later the heat capacity of hydrogen chloride was correctly calculated by Hutchisson.¹⁰

The entropy can be calculated very simply from the observed energy levels of molecules by a method to be given below, the principle of which is due to Tolman and Badger,¹¹ who, assuming rigid molecules, obtained expressions for the rotational entropy. Their paper unfortunately contains a number of errors in connection with the neglect of integration constants due to the multiple *a priori* probabilities of the zero state in several of their assumed cases.

It was shown by Giaque and Wiebe⁹ that the equation given by Tolman and Badger holds exactly for molecular entropy due to rotation-vibration or electron excitation, regardless of how irregular these levels might be.

The method is as follows

$$dS^\circ = \frac{dE^\circ}{dT} \cdot d \ln T \quad (8)$$

$$S^\circ - S_0^\circ = \int_0^T \frac{dE^\circ}{dT} \cdot d \ln T \quad (9)$$

$$= -R \int_0^T \frac{d}{dT} \frac{d \ln Q}{d \ln T} \cdot d \ln T \quad (10)$$

$$= R \left[\ln Q + T \frac{d \ln Q}{dT} \right]_0^T \quad (11)$$

$$= R \left[\ln Q_T - \ln Q_0 + T \frac{d \ln Q_T}{dT} \right] \quad (12)$$

$$= R \left[\ln \sum p e^{-\epsilon/kT} - \ln p_0 + \frac{1}{kT} \frac{\sum p e^{-\epsilon/kT}}{\sum p e^{-\epsilon/kT}} \right] \quad (13)$$

Particular attention is called to the term $-R \ln p_0$ in Equation 13 since this has been the cause of considerable misunderstanding. p_0 represents the number of states which have nearly the energy of the zero state and have thus been grouped together for convenience. However, this method leads to an assumed situation where even at the absolute zero of temperature the molecules are distributed equally between p_0 states, thus leading to a zero point entropy of $R \ln p_0$. The question as to whether this could actually happen at the unattainable absolute zero, infinite volume and zero magnetic and electric field strengths which would be necessary under equilibrium conditions need not seriously concern us in this case. $S_0^\circ = R \ln p_0$ and S° , the absolute entropy, is given by

⁹ Giaque and Wiebe, *THIS JOURNAL*, **50**, 101 (1928).

¹⁰ Hutchisson, *ibid.*, **50**, 1895 (1928).

¹¹ Tolman and Badger, *ibid.*, **45**, 2277 (1923). Urey, *ibid.*, **45**, 1445 (1923), essentially used this method by graphically integrating one of Relche's heat capacity equations.

$$S^\circ = R \left[\ln Q_r + T \frac{d \ln Q}{dT} \right] \quad (14)$$

This equation, which holds for all types of states which have been observed, is so general that it should hold for any that are likely to be discovered. This includes the multiplicities due to nuclear effects such as spin.

We believe it is desirable to give another, even simpler, derivation of the important Equation 14, which is the foundation of all the important equilibrium data which may be obtained from spectroscopic observations on molecules.

Let us consider a box with two compartments and a total volume such that it will hold one mole of an ideal gas at pressure P . Let one compartment be filled with gas 1 and the other filled with gas 2, each at pressure P . If the two gases are allowed to intermix uniformly, the entropy increase is given by¹²

$$\Delta S^\circ = -R (N_1 \ln N_1 + N_2 \ln N_2) \quad (15)$$

where N_1 and N_2 refer to the respective mole fractions of the two gases. In general when there are a large number of gases and corresponding compartments in the molal box, the expression for the increase in entropy on mixing becomes

$$\Delta S^\circ = -R(N_1 \ln N_1 + N_2 \ln N_2 + \dots N_r \ln N_r) \quad (16)$$

It is extremely useful to regard the various states among which molecules are distributed as supplying the basis for referring to different kinds of molecules in much the same manner as it is convenient to distinguish between optical isomers for some purposes. The number of the molecules in each of the states (excluding translation) is so large that it is convenient to think of a gas having such degrees of freedom as rotation, vibration and electron excitation as consisting of a mixture of a large number of kinds of gases, each kind being distinguished by its quantum numbers.

Let us imagine the molal box to be divided into a sufficient number of compartments of such volumes as are necessary to contain the equilibrium numbers of molecules of each kind or state (excluding translational states), at pressure P . Each of the compartments will contain what may be considered as a perfect monatomic gas. Each molecule within a given compartment is like every other within the same compartment except for the translational distribution. In such a case as that described, the total entropy is simply that of a monatomic gas. The entropy due to all other degrees of freedom in the equilibrium mixture is just the entropy associated with the uniform mixing of the various segregated portions. It may be well to emphasize in connection with the above statements that zero entropy with regard to a certain degree of freedom in no way implies that the molecules are necessarily all in the lowest energy state but only

¹² Lewis and Randall, Ref. 6, p. 440.

that all the molecules are in the same state, the "lack of randomness" of Lewis and Gibson.¹³

The entropy of mixing, referred to above, may be calculated as follows

$$N_0 = \frac{1}{Q}, N_1 = \frac{e^{-\epsilon_1/kT}}{Q}, \text{ etc.} \quad (17)$$

From Equation 16

$$\Delta S^\circ = -R \left[p_0 \times \frac{1}{Q} \ln \frac{1}{Q} + p_1 \times \frac{e^{-\epsilon_1/kT}}{Q} \ln \frac{e^{-\epsilon_1/kT}}{Q} + \dots \right] \quad (18)$$

$$= R \left[\ln Q + \frac{1}{kT} \frac{\sum p \epsilon e^{-\epsilon/kT}}{Q} \right] \quad (19)$$

$$= R \left[\ln Q + T \frac{d \ln Q}{dT} \right]$$

which is the previous equation (14). The significance of the p 's before the terms in Equation 18 is that there are p terms of equal mole fraction.

The Absolute Entropy.—The well-known equations for the translational entropy of a gas, for which references were given earlier, are

$$S^\circ = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V + \frac{5}{2} R + C \quad (20)$$

where M is the molecular weight, V the molal volume in cc. and $C = R \ln [(2\pi k)^{3/2}/h^3 N^{5/2}] = -16.024$ calories per mole per degree,¹⁴ where h is Planck's constant, and from the gas law

$$S^\circ = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P + \frac{5}{2} R + C + R \ln R \quad (21)$$

when P is the pressure in atmospheres. $C + R \ln R = -7.267$.

To obtain the absolute entropy the amount $R \ln Q + RT(d \ln Q/dT)$ must be added to either Equation 20 or 21.

The Calculation of Free Energy.—The free energy F is given by the equation⁶

$$F = H - TS \quad (22)$$

where the heat content

$$H = E + PV \quad (23)$$

For the ideal gas

$$H^\circ = E^\circ + RT \quad (24)$$

Then

$$F^\circ = E^\circ + RT - \frac{3}{2} RT \ln M - \frac{5}{2} RT \ln T + RT \ln P - \frac{5}{2} RT - CT - RT \ln R - RT \ln Q - RT^2 \frac{d \ln Q}{dT} \quad (25)$$

The total energy E° is equal to the sum of the energy at the absolute zero E_0° , the energy of translation $3/2 RT$, and the energy due to all other degrees of freedom $RT^2(d \ln Q/dT)$.

$$E^\circ = E_0^\circ + \frac{3}{2} RT + RT^2 \frac{d \ln Q}{dT} \quad (26)$$

¹³ Lewis and Gibson, Ref. 6, Chap. XXXI.

¹⁴ The values used for all natural constants are those given by "International Critical Tables," Vol. I, p. 16.

Combining Equations 25 and 26

$$F^\circ - E_0^\circ = -\frac{3}{2}RT \ln M - \frac{5}{2}RT \ln T + RT \ln P - CT - RT \ln R - RT \ln Q \quad (27)$$

When the necessary atomic or molecular energy levels are known, Q may be calculated for any desired temperatures and tables of $F^\circ - E_0^\circ$, or preferably $(F^\circ - E_0^\circ)/T$ may be prepared. By combination of these values for the various substances involved in a given reaction, the value of $\Delta(F^\circ - E_0^\circ)$ may be obtained. F° is the nomenclature of Lewis and Randall for the standard state, in this case, the hypothetical ideal gas state with $P = 1$ atmos.

$$\Delta F^\circ = -RT \ln K^{\ddagger} = \Delta(F^\circ - E_0^\circ) + \Delta E_0^\circ \quad (28)$$

From Equation 28 the equilibrium constant may be calculated for any desired temperature provided that ΔE_0° may be determined.

The Determination of ΔE_0° .—There are three general methods of evaluating ΔE_0° . (I) When the various excited states of a molecule are known up to dissociation into atoms, ΔE_0° is known for that reaction from spectroscopic data alone. By proper combinations ΔE_0° can then be obtained for other reactions. This method which gives great promise has already been applied to the dissociation of a number of diatomic molecules,¹⁵ while most existing calculations of this type are uncertain, due principally to considerable extrapolation, it seems certain that this difficulty will be minimized by future work on this relatively new method. In several cases where the extrapolation is small, the method already provides our best source of this information.

(II) ΔE_0° may be calculated by means of Equation 28, when one reliable value of the equilibrium constant is known, or if K is known over a range of temperatures, a more reliable value of ΔE_0° may be obtained by making use of the several data.

(III) When ΔH° is known from a calorimetric determination at temperature T , ΔE_0° may be obtained with the assistance of Equations 24 and 26.

$$\text{Thus } \Delta E_0^\circ = \Delta H^\circ - \Delta \left[\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} \right] \quad (29)$$

Equilibrium between Solids, Liquids and Gases.—There are many cases where it will be necessary to consider equilibrium between some condensed state or states and gases, for example



Here the third law of thermodynamics may be used for carbon in combination with spectroscopic observations on the gases. Thus

$$F^\circ - E_0^\circ = \int_0^T C_p dT - T \int_0^T C_p d \ln T \quad (30)$$

Recent values of this function are given by Rodebush and Rodebush.¹⁶

¹⁵ Birge, "International Critical Tables," 1929, Vol. V, p. 418.

¹⁶ Rodebush and Rodebush, "International Critical Tables," Vol. V, p. 87.

The F used in these tables is our $F^\circ - E_0^\circ$. These may be combined with the values of $F^\circ - E_0^\circ$ obtained for gases.

It is evident that the $F^\circ - E_0^\circ$ values for gases are of great utility even when no low temperature heat capacity measurements are available. However, as usual, this will necessitate the evaluation of at least one undetermined constant from equilibrium data.

In concluding these derivations, it is interesting to note that the exact determination of $F^\circ - E_0^\circ$ from spectroscopic data is a relatively easy calculation, involving only the summation of the Q series. The calculation of entropy or energy involves, in addition, the temperature derivative of the Q series, in which case the terms do not become negligible so rapidly.

The calculation of heat capacity involves the second derivative of the Q series, which is somewhat more laborious to sum. Fortunately the heat capacity need not be calculated in the process of determining an equilibrium and in many cases the entropy and energy may also be left undetermined.

The calculation of values of the free energy function to high temperatures is now in progress for the atoms and molecules for which the energy levels are known and it is expected that it will be possible to begin publication of this material in the near future.

Summary

Methods and equations for the *exact* calculation of free energy and other properties of the thermodynamic standard state of gases have been discussed.

A simple method of deriving a general expression for the absolute entropy of ideal gases has been given. This covers molecular rotation, vibration, electronic excitation and nuclear spin. In addition the method supplies a valuable insight into the simple relationship of complicated molecular states to the entropy.

The equations given will serve as the basis for an extended series of tabulations of free energy of gases based on available spectroscopic data.

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