The Density of Energy States in Solids

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FOR crystals or very complex molecules the energy levels are numerous and are either inherently or instrumentally unresolvable. As yet little progress has been made in devising methods of locating these levels although such information is of importance to any theory of molecular structure. In this note I wish to point out that a very general approach is available through the use of thermodynamic functions of the aggregate; further, to demonstrate that solutions exist for such equations which are experimentally indistinguishable from the ones specified by the data.

The sum-over-states may be readily computed from the entropy,

$$\log Z(T) = \frac{1}{kT}\int_0^T S(T)dT,$$

while

$$Z(T) = \sum_m g_m e^{-E_m/kT} \qquad (1)$$

is a fundamental definition of quantum statistical mechanics. The problem is reduced to an inversion of (1) so that $g_m(E_m)$ could be found once a $Z(T)$ is given. Clearly a rigorous solution is impossible even if the sum-over-states were known for all temperatures since, as $T \to \infty$, $Z(T) \to \infty$ very rapidly (in the order of T^N). Several of a number of possible approximations are briefly discussed below.

A. The function $Z(T)$ is continuous, finite, single valued and specified over the region $(0, T_1)$. However, it may have a discontinuous first derivative at temperatures at which the substance undergoes a change of phase. One may therefore approximate it to within any prescribed accuracy by a polynomial in T in the above range.

$$Z(T) = \sum_n a_n T^{n+1}, \quad Z(0) = 0.$$

The change of variable $T = 1/s$ results in

$$Z(1/s) = Y(s) = \sum_n a_n (1/s)^{n+1}$$

so that $Y(s)$ is analytic in the interval (s^1, ∞).

Now, Eq. (1) may be rewritten in the form

$$Y(s) = \int_0^\infty g(E)e^{-sE/k}dE \qquad (2)$$

where $g(E)$ is the desired density function. The change from the sum to the integral is permissible because of the closely spaced energy levels. Since for all s whose real part is positive

$$(1/s)^{n+1} = \int_0^\infty e^{-sE/k}E^n/(n!k^{n+1})dE,$$

Eq. (2) is satisfied by

$$g(E) = \sum_n a_n E^n/(n!k^{n+1}) \quad \text{for } s \geqslant s_1.$$

Therefore a solution for (2) exists for all $s \geqslant s_1$.

B. If the range $0 \leqslant s \leqslant \infty$ is desired, an equation approximating (2) must be treated. Introduce the function

$$Y(s+s_1) = \sum_n a_n (1/s+s_1)^{n+1}$$

which is analytic for $s \geqslant 0$. The necessary and sufficient conditions that a solution for

$$Y(s+s_1) = \int_0^\infty kg(E)e^{-s(E/k)}d(E/k) \qquad (3)$$

exists are then satisfied (inversion by means of the Laplace transform[1]). It follows that if the maximum temperature for which $Z(T)$ is known is large—i.e. s_1 is sufficiently small—so that $Y(s+s_1)$ may be identified with $Y(s)$ to within the accuracy of the data, that solution could be accepted also for (2). One should keep in mind that often for $T \gg \theta$, a safe extrapolation of $S(T)$ to larger T may be made.

C. Write Eq. (1) in the form

$$Z(T) = \int_{E_0}^{\beta kT} g(E)e^{-E/kT}dE;$$

E_0 describes the ground state. The approximation enters in replacing the upper infinite limit by

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[1] D. V. Widder, Trans. Am. Math. Soc. **36**, 116 (1934).

βkT where β is a very large number, of such magnitude as to make $\int_{\beta kT}^{\infty} g(E)e^{-E/kT}dE$ negligible.

A change of variable $\beta kT = t$ transforms the above into a Volterra integral equation of the first kind,

$$Z(t/\beta) = \int_{E_0}^{t} g(E)e^{-\beta E/t}dE \qquad (4)$$

with $E_0 \leqslant E \leqslant t \leqslant \beta kT_1$. Integration by parts or a differentiation leads to an equation of the second kind for which a unique continuous solution exists, in the latter case provided $Z(E_0/\beta) = 0$.[2] This will be almost true if β is taken sufficiently large; actually, the solution found will be for the equation

$$\mathbf{Z}(t/\beta) - \mathbf{Z}(E_0/\beta) = \int_{E_0}^{t} g(E)e^{-\beta E/t}dE,$$

where $\mathbf{Z} = Z$ except in that the discontinuities in the derivative of Z if there are any, have been smoothed over.

I have undertaken the application of these suggestions to the case of diamond for which accurate specific heat data have recently been published.[3] Pitzer found that the experimental curve lies between the one predicted using the continuous solid model and that deduced from the three-dimensional lattice theory of Blackman.

[2] G. Kowalewski, *Integralgleichungen* (Gruyter, 1930).

[3] K. S. Pitzer, J. Chem. Phys. **6**, 68 (1938).

A Note on the paper by J. N. Pearce and Lyle R. Dawson on "The Influence of Salts on the Absorption Spectra of Aqueous Cobalt Chloride Solutions"

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SINCE in the recent paper of J. N. Pearce and Lyle R. Dawson,[1] the inadequacy of existing explanations of the well-known color changes in cobalt chloride solutions has been mentioned, the present author wishes to show that his explanation put forward eight years ago[2] cannot be regarded as an unsatisfactory one for the experiments given by the above named authors.

The explanation of the present author is based on a polarigraphic study of current-voltage curves obtained in electrolysis of cobalt chloride solutions with the dropping mercury cathode, as well as on spectroscopic research. Through these investigations it has been proved that cobalt deposits at the dropping mercury cathode from blue solutions with a large concentration of calcium chloride at a more positive potential than it does from the pure pink water solutions. Further, while the current-voltage curves in the latter case do not conform to the expected equation for the deposition of a divalent metal, the deposition from the blue cobaltous solutions proceeds according to this equation. The deviation from this equation has been explained as being due to the slowness of dehydration of cobaltous ions, which takes place at the surface of the cathode in order to deposit metallic cobalt. The easier deposition from blue solutions in which a blue complex $[CoCl_n]^{(n-2)-}$ has to be assumed, is imagined to be facilitated by the ease of splitting of such a complex into free cobaltous ions.

These facts led the present author to the conclusion that the effect of the addition of a large excess of calcium chloride in the hydrated pink cobaltous ions is twofold: 1. The activity of water is lessened and thus the concentration of dehydrated cobaltous cations is increased, 2. the

[1] J. N. Pearce and Lyle R. Dawson, J. Chem. Phys. **6**, 128 (1938).
[2] R. Brdička, Coll. Czechoslov. Chem. Comm. **2**, 489 and 545 (1930).