TABLE I

EQUILIBRIUM CONSTANTS AND EQUILIBRIUM PRESSURES OF BORINE, FOR THE REACTION $2BH_3 = B_2H_6$

T, °K.	K (at.$^{-1}$)	K (m./cc.$^{-1}$)	P_{BH_3} (at.)	P_{BH_3} (mm.)
273	1.73×10^{18}	3.88×10^{22}	$1.48 \times 10^{-9}\sqrt{P_{at}}$	$4.1 \times 10^{-8}\sqrt{P_{mm}}$
300	8.57×10^{15}	2.11×10^{20}	$2.16 \times 10^{-8}\sqrt{P_{at}}$	$6.0 \times 10^{-7}\sqrt{P_{mm}}$
373	2.34×10^{11}	7.16×10^{16}	$4.14 \times 10^{-6}\sqrt{P_{at}}$	$1.1 \times 10^{-4}\sqrt{P_{mm}}$
473	2.54×10^{7}	0.99×10^{12}	$1.99 \times 10^{-4}\sqrt{P_{at}}$	$5.5 \times 10^{-3}\sqrt{P_{mm}}$

0.1 e.u./mole, at 300°K. and one atmosphere. Using the frequency assignments for diborane as given by Anderson and Barker[4] we computed a vibrational contribution of 2.34 ± 0.1 e.u. A planar structure was assumed for BH_3, with a B–H distance equal to 1.16 Å. Badger's rule was then used to estimate the stretching force constant,[5] and various interpolations made to estimate the bending and interaction force constants. These led to a total entropy for BH_3 at 300°K. and one atmosphere of 44.9 ± 0.2 e.u. Thus for the association reaction, $\Delta S^\circ_{300} = -33.78$ e.u./mole of diborane. To the precision dealt with here one may neglect the specific heat correction and consider the enthalpy change independent of the temperature. Thus, $\log (K_{eq})_{atm} = -7.38_4 + (6995/T)$. Typical values for four temperatures are listed in the table. Clearly the equilibrium concentrations of borine are too small to be detected by the usual physical techniques.

We have also deduced an upper limit for the bimolecular rate constant (k') for the association of two borines. Burg[6] recently reported on the kinetics of the decomposition of borine carbonyl. He concluded that the mechanism of the reaction is as follows:

$$\text{(a)} \qquad BH_3CO = BH_3 + CO \quad K'_{eq}$$

$$\text{(b)} \qquad BH_3 + BH_3CO \longrightarrow B_2H_6 + CO \quad k$$

Hence, during the approach to equilibrium, both the inverse of (a), and step (b), must proceed faster than does the association:

$$\text{(c)} \qquad 2BH_3 \longrightarrow B_2H_6 \quad k'$$

That is, the correctness of Burg's mechanism implies the inequality

$$k'(BH_3)^2 < k(BH_3)(BH_3CO)$$

Using the equilibrium condition on the first step of the borine decomposition (a), this reduces to

$$k' < k(P_{tot}/K'_{eq})^{1/2}$$

ΔH° for (a) was obtained by combining the ΔH° for the over-all borine carbonyl decomposition as given by Burg with our value for the heat of dissociation of diborane. The entropy change for step (a) was obtained by subtracting the computed entropy of H_3BCO—as based on the structural data of Gordy[7] and spectral data of Cowan[8]—from the now known entropy of borine and carbon monoxide.[9] Thus K'_{eq} was computed. The resulting condition on the rate constant is

$$k' < 5 \times 10^9 \text{ cc./mole/sec.}$$

Such a value for a second order rate constant suggests an activation energy of about 5 kcal./mole. It is indeed very interesting to compare the following rate constants:

$$\begin{array}{lll} k & = 1.98 \times 10^6 \text{ cc./mole/sec.}; & E_a \cong 6.8 \text{ kcal./mole} \\ k' & < 5 \quad \times 10^9 & E_a \sim 5 \\ k'' & = 6.4 \quad \times 10^9 & E_a \cong 6 \end{array}$$

The last value is for the displacement reaction

$$BH_3 + B_2D_6 = BH_3BD_3 + BD_3 \quad k''$$

as reported by Koski.[10]

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[4] W. E. Anderson and E. F. Barker, *J. Chem. Phys.*, **18**, 698 (1950).

[5] The force constant deduced is 3.38×10^5 dynes/cm. This compares with 3.21 and 3.42×10^5 reported for the B–H stretching force constant in H_3BCO and $B_3N_3H_6$, respectively.

[6] A. Burg, THIS JOURNAL, **74**, 3482 (1952).

[7] W. Gordy, H. Ring and A. Burg, *Phys. Rev.*, **78**, 512 (1950).

[8] R. D. Cowan, *J. Chem. Phys.*, **18**, 1101 (1950).

[9] H. L. Johnson and C. O. Davis, THIS JOURNAL, **56**, 271 (1934).

[10] W. S. Koski, private communication.

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THERMODYNAMIC FUNCTIONS FOR SURFACES OF CRYSTALS

Sir:

Recently a method[1] was described for the determination of thermodynamic quantities of surfaces of solids which appears to be beautiful in its simplicity, and extremely general in its application. Besides the surface area, the measurements required are the differences in the heats of solution and in the heat capacities of a finely divided sample and one composed of very large crystals. It is regrettable that these authors omitted to call attention to an *essential pragmatic test* for the applicability of their method. Since the enthalpy, entropy and surface free energy are *extensive* properties their magnitudes per unit area should be *independent* of *crystallite size and shape.* The preliminary results quoted by Jura and Garland for magnesium oxide have not been subjected to this test. What, then, may we anticipate when a complete set of data becomes available for a well crystallized substance?

First let us assume that regardless of the temperature and crystallite size, the structure of the crystals is geometrically perfect,[2] and their surface is absolutely free of adsorbed gases. Nevertheless the thermodynamic functions for the surface for two samples with the same total area will differ *unless* they have the same proportions of area contributed by faces of different crystallographic indices. This is based on the established facts that faces with different indices have different characteristics for adsorption,[3] catalysis,[4] and reaction.[5]

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[1] G. Jura and C. W. Garland, THIS JOURNAL, **74**, 6033 (1952).

[2] This is equivalent to the statement that such a structure is determined by the criterion of minimum enthalpy only.

[3] For example, T. N. Rhodin, Jr., THIS JOURNAL, **72**, 5691 (1950).

[4] O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

[5] T. N. Rhodin, Jr., THIS JOURNAL, **73**, 3143 (1951).

Also, theoretical estimates indicate they differ in surface free energy.[6] One may argue with justification that precise values for the surface thermodynamic quantities for a polycrystalline sample cannot be conceptually defined without specifying a shape distribution function and proving that it is invariant with crystal size, for each substance studied. In addition, there are numerous experiments which suggest that the thermodynamic potential of material in small regions surrounding corners, edges and steps on crystal faces differs from that in geometrically plane surfaces. Since the number of such corners, edges, etc., is proportional to the number of crystals, whereas the total area depends on that number times the square of the linear extension of the crystals [so that for a mole of substance divided into n particles of uniform size, $S \propto (M/\rho)^{2/3}n^{1/3}$], it is clear that any macroscopic quantity which depends on the thermodynamic potential will not be strictly extensive with respect to surface area. As a matter of fact, in a very interesting paper preceding the one under discussion, one of the authors (G. J.) and K. S. Pitzer[7] showed that at low temperatures a significant contribution to the specific heat of *very* small particles comes from the gross motion of the particles; *i.e.*, their heat capacity depends on the *number* of *particles*, in addition to the differences between the vibrational frequencies of atoms in the surface layers and those in the bulk crystal.

In a discussion of the thermodynamic properties of surfaces, one should recognize, however, that even under conditions approaching ideality in composition and configuration, the structures of crystals at temperatures other than 0°K. is determined by minimizing their total free energy.[8] This implies that there must be an entropy contribution arising from lattice defects. Such imperfections will affect the enthalpy as well (and hence the heat of solution), and the magnitude of the increment will depend on crystallite size; it is unlikely that the net effect of the various types of possible defects will in the aggregate depend precisely on the square of the linear extension of the crystals. Indeed, in most laboratory procedures for the preparation of crystals strains, distortions, minute amounts of impurity, etc., will be introduced.[9] Finally, the practical problem of the complete elimination of adsorbed gases will be difficult to solve. We may conclude that the application of the thermodynamic method of Jura and Garland to well crystallized materials will lead to values for thermodynamic functions which only in part are due to the presence of surface. Such magnitudes will be *extensive* with respect to surface area only when the method of preparation, crystal size and shape distributions, etc., are kept strictly unaltered. Such a restriction nullifies the power of the thermodynamic method.

The proposal of Jura and Garland does apply to liquids and glasses, for which the inherent randomness of internal structural minimizes the relative contributions of the very factors which vitiate the method for well crystallized materials.

It is a pleasure to acknowledge an interesting discussion of this paper with Prof. J. A. Krumhansl, Department of Physics.

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[6] R. Shuttleworth, *Proc. Phys. Soc.*, **A62**, 167 (1949); W. D. Harkins, *J. Chem. Phys.*, **10**, 268 (1942). Also, see the excellent summary "Use of Classical Macroscopic Concepts in Surface Energy Problems" by Conyers Herring, presented at a conference on "Structure and Properties of Solid Surfaces", September, 1952, Intn. Union Pure and Applied Physics.

[7] G. Jura and K. S. Pitzer, THIS JOURNAL, **74**, 6030 (1952).

[8] N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Clarendon Press, Oxford, 1948, Chap. II.

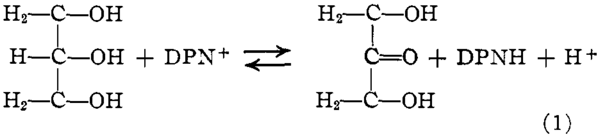
[9] See Chapter IV, ref. 8; W. Shockley, "Electrons and Holes in Semiconductors," D. Van Nostrand Co., New York, N. Y., 1950.

A DPN SPECIFIC GLYCEROL DEHYDROGENASE FROM *AEROBACTER AEROGENES*[1]

Sirs:

A number of microörganisms have been shown to utilize glycerol as the sole carbon source.[2] The major product in the oxidation of glycerol in *Acetobacter suboxydans* has been shown to be dihydroxyacetone (DHA).[3] In *A. aerogenes* glycerol is oxidized past the DHA stage; the products are, in part, organic acids.[2b,4]

We have found that oxidation of glycerol in cell-free extracts of *A. aerogenes* requires diphosphopyridine nucleotide (DPN). This reaction can be followed spectrophotometrically at 340 mμ as shown in Fig. 1. Glycerol was incubated with DPN in the presence of dialysed cell-free extracts of *A. aerogenes*. After the reaction had approached equilibrium, DHA was added and the reaction that followed was due to the oxidation of the reduced DPN (DPNH) by the reduction of DHA to glycerol. Equation 1 expresses this relation as



$$\begin{array}{l} H_2\!-\!C\!-\!OH \\ \quad\;\; | \\ H\!-\!C\!-\!OH \\ \quad\;\; | \\ H_2\!-\!C\!-\!OH \end{array} + DPN^+ \rightleftarrows \begin{array}{l} H_2\!-\!C\!-\!OH \\ \quad\;\; | \\ \quad\;\; C\!=\!O \\ \quad\;\; | \\ H_2\!-\!C\!-\!OH \end{array} + DPNH + H^+ \qquad (1)$$

Reaction 1 proceeds with glycerol in the presence of hydroxylamine which inhibits alcohol dehydrogenase activity.[5] This, therefore, indicates that the glycerol dehydrogenase is a separate enzyme distinct from alcohol dehydrogenase.

At comparable concentrations glyceraldehyde is reduced at a slower rate than DHA. This would suggest that DHA is the primary product of glycerol oxidation by DPN in *A. aerogenes*. Neither α- or β-glycerol monophosphates are oxidized by this enzyme preparation. Triphosphopyridine nucleotide (TPN) is inactive as a substitute for DPN in reaction 1.

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[1] Contribution No. 37 of the McCollum-Pratt Institute. This work was supported in part by grants from the Rockefeller Foundation and the American Cancer Society as recommended by the Committee on Growth of the National Research Council.

[2] (a) H. R. Braak, Thesis, Delft, 1928; (b) R. E. Buchanan and E. I. Fulmer, "Physiology and Biochemistry of Bacteria," The Williams and Wilkins Company, Baltimore, Md., 1930, Vol. III, p. 248.

[3] A. J. Kluyver and F. J. G. DeLeeuw, *Tijdschr. Vergelijk. Geneesk.*, **10**, 170 (1924); L. A. Underkofler and E. I. Fulmer, THIS JOURNAL, **59**, 301 (1937).

[4] H. Kumagawa, *Biochem. Z.*, **131**, 156 (1922); A. C. Baskett and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **B138**, 75 (1951).

[5] N. O. Kaplan and M. M. Ciotti, *J. Biol. Chem.*, in press.