tion, could not be prepared without virtual destruction of the specimen. For the present, the exact origin of these diopsidic reaction rims remains obscure.

R. A. Binns

Department of Geology, University
of New England, Armidale,
New South Wales, Australia

References and Notes

1. R. A. Binns, *Earth Planetary Sci. Letters* **2**, 23 (1967).
2. British Museum BM66200.
3. C. Frondel, *Dana's System of Mineralogy* (Wiley, New York, ed. 7, 1962), vol. 3.
4. Fe < 0.03 percent, Mn < 0.02 percent, Mg < 0.01 percent, Ca < 0.02 percent, Na < 0.2 percent.
5. In the British Museum (Natural History), the American Museum of Natural History, and the U.S. National Museum.
6. F. H. Snow, *Science* **16**, 38 (1890); G. F. Kunz and W. Weinschenk, *Tschermaks Mineral. Petrog. Mitt.* **12**, 177 (1891).
7. P. R. Busbeck, B. Mason, H. B. Wiik, *Geochim. Cosmochim. Acta* **30**, 1 (1966).
8. W. Wahl, *ibid.* **2**, 91 (1952).
9. M. Christophe-Michel-Lévy and H. Curien, *Bull. Soc. Franç. Minéral. Crist.* **88**, 122 (1965).
10. J. DeFelice, G. G. Fazio, E. L. Fireman, *Science* **142**, 673 (1963).
11. K. Fredriksson, P. S. De Carli, A. Aaramäe, in *Space Science III*, W. Priester, Ed. (North-Holland, Amsterdam, 1963).
12. W. Wahl, *Geochim. Cosmochim. Acta* **27**, 1025 (1963).
13. R. A. Binns, *Nature* **213**, 111 (1967); R. Knox, *Geochim. Cosmochim. Acta* **27**, 261 (1963).
14. Other black chondrites containing cavities include Hayes Center, Lawrence, McKinney, and Wickenberg.
15. R. Kretz, *J. Geol.* **71**, 773 (1963).
16. K. Keil and K. Fredriksson, *J. Geophys. Res.* **69**, 3487 (1964).
17. H. G. Wilshire, *Amer. J. Sci.* **259**, 260 (1961); J. F. G. Wilkinson, *J. Petrol.* **3**, 192 (1962).
18. N. L. Bowen, *Amer. J. Sci.* **38**, 207 (1914); E. F. Osborn and D. B. Tait, *ibid.* Bowen volume, p. 413 (1952); E. M. Levin, C. R. Robbins, H. F. McMurdie, *Phase Diagrams for Ceramists* (Amer. Ceramic Soc., Columbus, Ohio, 1964).
19. C. B. Clark, *J. Amer. Ceram. Soc.* **29**, 25 (1946).
20. Work done at the British Museum (Natural History), London. I thank S. J. B. Reed for electron-probe microanalyses, R. D. Tanner for the photography, and Brian Mason for reading the manuscript.

10 March 1967

Surface Tension and Surface Structure of Water

Abstract. *The surface tension–temperature relationship for water is smooth and linear when account is taken of the expansion of the surface with temperature. This plot permits the calculation of thermodynamic properties for 1 square centimeter of surface. Molar surface quantities are derived by assuming a hexagonal water surface structure.*

A basic knowledge of the nature of water surfaces is needed in several scientific pursuits dealing with evaporation from reservoirs, growth and coalescence of cloud droplets, and solubilization of oxygen in lakes, and for water-treatment processes dependent upon reactions involving dissolved oxygen. The most well known property of the surface is its tension, yet so elementary a subject as the relationship of surface tension and temperature is poorly understood. A good understanding of this relationship is needed for the calculation of the thermodynamic properties of the surface.

A re-analysis of some earlier data on water surface tension (*1*), along with some data recently obtained in this laboratory, has been made on the basis of some concepts first developed by Eötvös (*2*) and expanded by Ramsay and Shields (*3*). This method of analysis has the unique characteristic of permitting the calculation of extensive surface properties as a function of temperature for an amount of surface that always contains the same number of molecules. The surface layer of molecules is believed and assumed to expand with temperature in the same ratio as does the interior liquid. The volume expansion of the interior liquid varies as the reciprocal of the density, d, of the liquid. The surface area of the top layer is assumed, correlatively, to expand as the reciprocal of the bulk liquid density raised to the two-third power. Thus, one should be able to calculate the extensive surface property of surface free energy for a certain fixed number of molecules by dividing surface tension, γ, by $d^{2/3}$. The number of molecules under identification and measurement is that number composing 1 cm^2 of surface at 4°C; for, in dividing by $d^{2/3}$, one implicitly assumes that the 4°C-area, when the density is 1.0000, is the fixed unit area under consideration. The quantity $\gamma/^{2/3}$ is the surface free energy ΔG_s in ergs for this number of molecules.

The three sets of surface tension data were obtained by three different methods: Moser, by the ring mehod; Teitel'baum, by the maximum bubble pressure method; and Claussen, by rise in a capillary of 0.30 mm diameter. The first two sets of data were for tensions of water in contact with air, while Claussen's is for water in contact with helium. The Moser and Claussen data were normalized linearly to agree with the Teitel'baum data at 25°C, in order to eliminate systematic errors in calibration or measurement.

The method of plotting the surface tension data follows from standard practice in chemical thermodynamics. A consideration of the equation

$$\Delta G_s = \Delta H_s - T\Delta S_s \qquad (1)$$

where ΔG_s $(= \gamma/d^{2/3})$, ΔH_s, and ΔS_s are the free energy, heat, and the en-

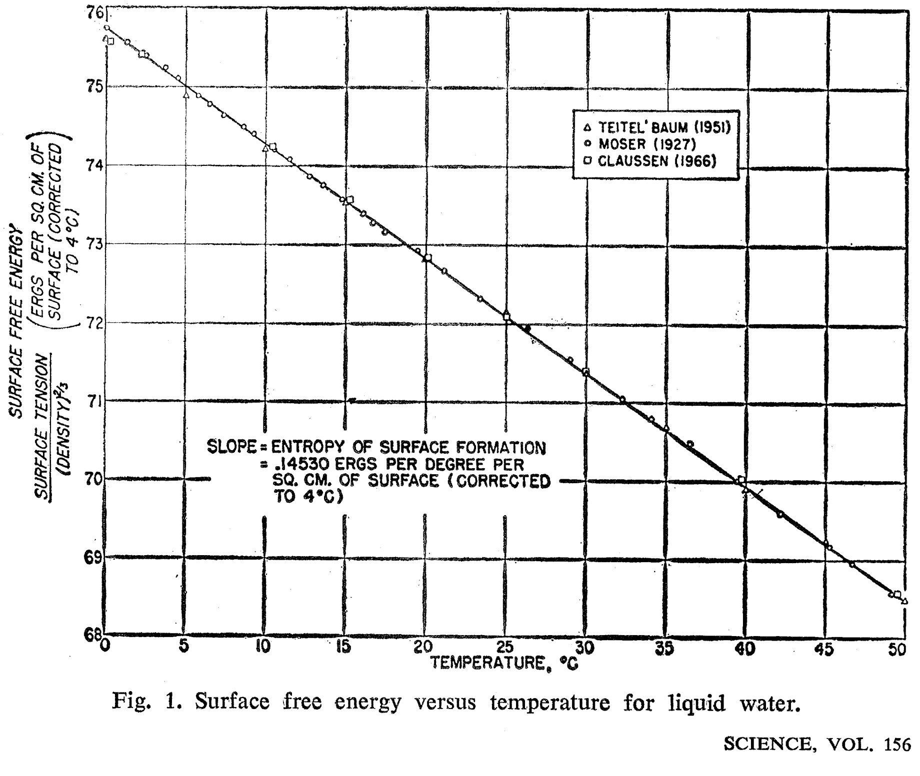

Fig. 1. Surface free energy versus temperature for liquid water.

tropy of surface formation, respectively, reveals two equivalent methods of plotting the surface tension data:

$$\frac{\gamma}{d^{2/3}} = \Delta H_s - T\Delta S_s \qquad (2)$$

$$\frac{\gamma/d^{2/3}}{T} = \Delta H_s \left(\frac{1}{T}\right) - \Delta S_s \qquad (3)$$

A plot of $\gamma/d^{2/3}$ against T(°C) possesses a slope of $-\Delta S_s$, shown in Fig. 1. A plot of

$$\frac{\gamma/d^{2/3}}{T, °\mathrm{K}} \text{ against } \frac{1}{T, °\mathrm{K}}$$

possesses a slope of ΔH_s, shown in Fig. 2.

The linearity of these plots is clearly evident. The Moser data were further subjected to least-squares analysis and the standard deviation from a straight line was 0.04 percent, which is less than one-half of his claimed error of 0.1 percent. The main part of the data of Teitel'baum and the main part of my data were found to be within 0.05 percent of this Moser best-fit line; the larger negative deviations of a few low temperature points, clearly evident in Fig. 1, may be suspect of influence by impurities. There was no statistically significant tendency for curvature in the Moser data; this data seemed of highest quality.

This smooth linear plot is in sharp contrast to recent speculations (*4*) that the surface tension may possess discontinuous variations with temperature.

The least-squares analysis of the data shown in Figs. 1 and 2 permits one to give the following assessment of the three extensive thermodynamic properties on the basis of the 4°C-cm² quantity of surface:

$$\Delta G_S = +\ 75.74 \text{ erg/4°-cm}^2 \text{ (at 0°C)}$$
$$\Delta H_S = +\ 115.42 \text{ erg/4°-cm}^2$$
$$\Delta S_S = +\ 0.14530 \text{ erg/°K/4°-cm}^2$$

Substitution of these values into Eqs. 2 and 3 gives the following best-fit equations for the plots in Figs. 1 and 2, respectively.

$$\frac{\gamma}{d^{2/3}} = 75.74 - 0.14530\,T, °\mathrm{C} \qquad (4)$$

$$\frac{\gamma/d^{2/3}}{T, °\mathrm{K}} = 115.42 \left(\frac{1}{T, °\mathrm{K}}\right) - 0.14530 \qquad (5)$$

If one should later decide that another absolute value of surface tension is more correct than the Teitel'baum value chosen as standard for the calculations above, then one would be required to make the same percentage change in all calculated constants of the equations. This follows from the assumption that all corrections in surface tension involve the same linear constant, or $\gamma_{\mathrm{corr.}} = \gamma_{\mathrm{Teitel.}}$ multiplied by a constant. With Moser's possibly more precise value of 72.87 dynes/cm for the surface tension at 18°C, $\gamma/d^{2/3}$ becomes 72.94, and the more exact constants for the equations become 0.26 percent smaller in magnitude:

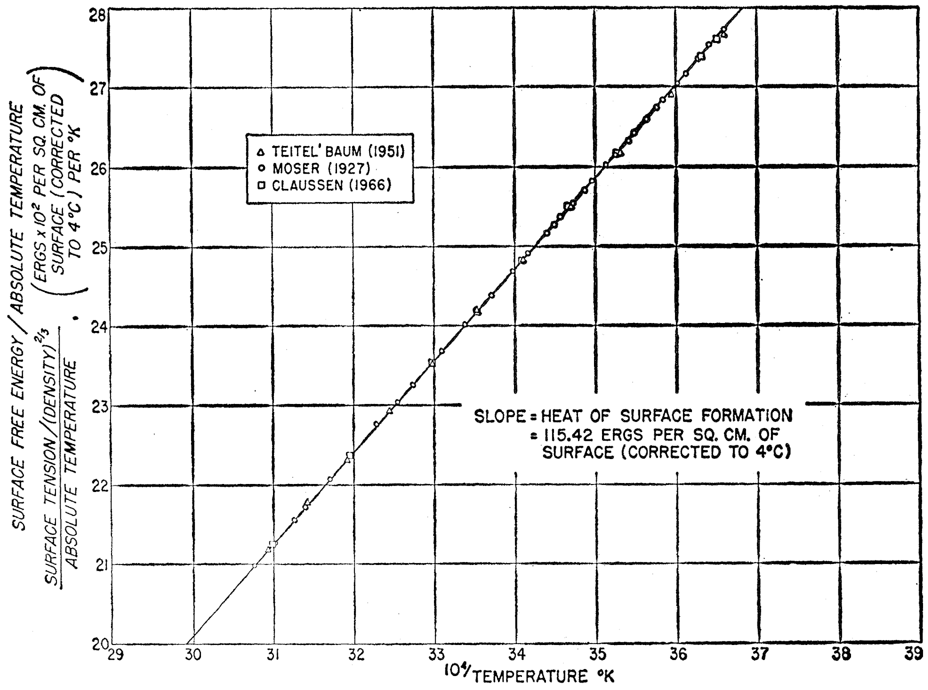

Fig. 2. Surface free energy divided by the absolute temperature versus the reciprocal of the absolute temperature for liquid water.

$$\Delta G_S = +\ 75.54 \text{ erg/4°-cm}^2 \text{ (at 0°C)}$$
$$\Delta H_S = +\ 115.12 \text{ erg/4°-cm}^2$$
$$\Delta S_S = +\ 0.14492 \text{ erg/°K/4°-cm}^2$$

The molar surface area may be determined by assuming with Guastalla (*5*) that (i) the surface is identical to a puckered hexagonal plane as found in ordinary ice, a plane normal to the *c* axis, and that (ii) only half of these molecules are exposed surface molecules with residual, unsatisfied valences. The surface area per surface molecule, which is identical to per unit hexagon, then becomes about 19.5 × 10^{-16} cm², and the molar surface area becomes 1.1745 × 10^{9} cm². The molar thermodynamic quantities then become

$$\Delta G_S = +\,2120 \text{ cal/mol of surface at (0°C)}$$
$$\Delta H_S = +\,3231 \text{ cal/mol of surface}$$
$$\Delta S_S = +\,4.067 \text{ e.u./mol of surface}$$

These molar quantities will be further refined when the exact interatomic distances and angles in the surface are known.

The figure of 19.5 Å² area is a characteristic of many investigations of fatty acid films, this being approximately the area of one fatty acid molecule adsorbed on the surface. This figure was originally attributed also to a characteristic of water structure by Guastalla (*5*). It is my opinion that this fact has been neglected, that not only the area of the fatty acid molecule but also the water structure contributes to this common 19.5 Å² area determination, and that the use of film pressure data may permit an accurate assessment of the dimensions of surface water structure. By this means it is believed that one may be able to determine the proportionality factor between thermodynamic properties for one 4°C-cm² of surface and one mole of surface, thus permitting the calculation of precise molar surface properties.

WALTER F. CLAUSSEN
Illinois State Water Survey,
Box 232, Urbana 61801

References and Notes

1. H. Moser, *Am. Physik* **82**, 993 (1927); B. Ya. Teitel'baum, T. A. Gortolova, E. E. Sidorova, *Zh. Fiz. Khim.* **25**, 911 (1951); *Chem. Abstr.* **46**, 2884b (1952).
2. R. Eötvös, (Wied.) *Ann. Physik* **27**, 448 (1886).
3. W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London* **A184**, 647 (1893).
4. W. Drost-Hansen, *Ind. Eng. Chem.* **57**, 18 (1965).
5. J. Guastalla, *J. Chim. Phys.* **44**, 306 (1947).
6. I thank Dr. T. E. Larson for his interest in this problem, and Dr. James C. Neill for his efforts in the mathematical curve-fitting application.

27 February 1967