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are known. As the matrix B ranges over the real orthogonal n-dimensional (rotation) group all the possible solutions are obtained. The present method provides a systematic approach to the study of these solutions in indeterminate cases. It may then be possible to select the optimum solution on the basis of other considerations.

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[1] P. Torkington, J. Chem. Phys. **17**, 357 (1949).
[2] G. Glockler and J. Y. Tung, J. Chem. Phys. **13**, 388 (1945).
[3] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941).
[4] The order in which the "frequencies," λ_i, are arranged on the diagonal of Λ is immaterial, since F is invariant to a permutation of the λ_i's *accompanied by an equivalent permutation of the normal coordinates* (i.e., the columns of K, or B).

Use of Radiotracers to Measure Surface Adsorption from Mixtures

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July 27, 1950

A METHOD for using a radiotracer to measure the adsorption of a soluble surface-active agent at the solution-air interface has been developed in this laboratory[1,2] and has since been used elsewhere.[3] The method depends upon the fact that the radiation counted at the surface of a solution containing a soft beta-ray emitter is principally radiation from atoms which are near the surface of the solution. The measurements previously reported have been an adsorption isotherm for di-n-octyl sodium sulfosuccinate (Aerosol OTN)[1,2] and a single measurement for sodium octadecyl sulfate.[3] In both cases the agent was tagged with S^{35}.

A considerable number of measurements have now been carried out determining the adsorption of Aerosol OTN from solutions containing mixtures of Aerosol OTN with various inorganic salts and with alcohols, esters, or acids related to Aerosol OTN. The amount of Aerosol OTN adsorbed was not changed very much except when the second compound was also a surface-active agent.

The study of mixtures of Aerosol OTN with another similar surface-active agent, di-(2-ethyl hexyl) sodium sulfosuccinate (Aerosol OT), has provided some interesting data which are presented in Fig. 1. Varying amounts of Aerosol OT were added to solutions containing 3.2×10^{-6} molar Aerosol OTN (a concentration below the knee of the isotherm[1,2] and below the micelle point), and the surface adsorption was measured at 24°C. As the Aerosol OT concentration was increased, the Aerosol OTN on the surface was reduced, apparently being replaced by Aerosol OT. The equilibrium concentration of Aerosol OTN after formation of the surface layer varied from 2.3×10^{-6} molar to 3.2×10^{-6} molar. While the comparison should preferably have been made at constant equilibrium concentration of Aerosol OTN rather than at constant initial concentration, the experiment shows how

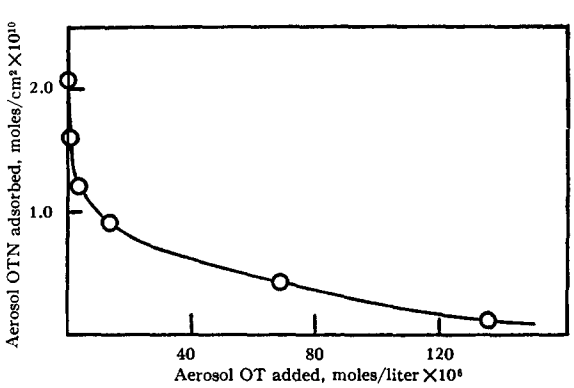

Fig. 1. Aerosol OTN adsorbed from mixtures with Aerosol OT containing 3.2×10^{-6} molar Aerosol OTN.

the radioactive tracer method can be used to measure the surface adsorption of one or more species in a mixture of surface-active agents. Surface tension measurements, conventionally used to measure surface adsorption, do not permit ready interpretation of results obtained in mixtures.

[1] Dixon, Weith, Argyle, and Salley, Nature **163**, 845 (1949).
[2] Salley, Weith, Argyle, and Dixon, Proc. Roy. Soc (to be published).
[3] Aniansson and Lamm, Nature **165**, 357 (1950).

The Isothermals of Rocksalt from Its Thermal Expansion

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July 3, 1950

THE usual calculations of the equation of state of solids are based on some pre-assumed form of the potential curves between pairs of atoms.[1,2] It would, however, be much simpler to use the thermal expansion data for this purpose as this would obviate the necessity of any assumption regarding the accuracy of the Debye theory or of the potential expression. The isothermals of rocksalt drawn on this basis are reproduced in Fig. 1. The

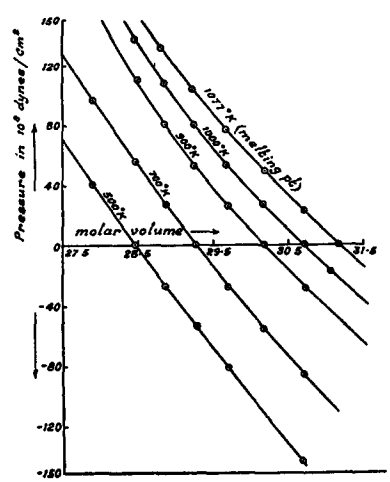

Fig. 1. Isotherms of rocksalt calculated from the thermal expansion.

method used by the writer is based on the evaluation of p_2, the part of the pressure due to the thermal vibrations from the Gruneisen constants at the appropriate volumes. The values of p_1, i.e., $\partial(N\phi/2)/\alpha V$ the part of pressure due to a static lattice, are obtained from the condition that at the volumes observed at different temperatures, $p_1+p_2=0$. For evaluating volumes at different temperatures, V_0 is assumed to be equal to 26.72. The Gruneisen constants at different volumes have been calculated from the thermal expansion data of Walther[3] by the usual relation,[4]

$$\gamma=\frac{\alpha V_0}{C_v K_0}\left(1-\frac{m+n+3}{6}\gamma\frac{K_0E}{V_0}\right)^2. \quad (1)$$

For evaluating the quantity within the brackets we have used $E=RT$, $(m+n+3)/6=2$ and the mean value of $\gamma=1.65$ as given in Gruneisen's article.

Compressibilities have been calculated from the slope of the curves and show a fair agreement with experimental values[5] (Table I). The agreement is liable to some improvement by a suitable modification of the evaluation of the bracket quantity in Eq. (1).

The values of p_1 calculated from the expansion data as indicated above are less than those evaluated from the expression for potential due to Huggins and Mayer [6]

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TABLE I. Compressibility of rocksalt at different temperatures in 10^{-13} cm²/dyne.

Temperature °K	Experimental k Adiabatic	Isothermal	k calculated from curves
500	47.6	52 6	50
600	50 1	56	52
700	54.1	62	56
800	59.3	68	58
900	61.4	72	63
1000	65.7	85	73
1070	63.7	89	76

The method can be used at low temperatures where the bracket quantity is unimportant. The experimental values of C_v, E, and α can be used, so that the results become independent of any theory of crystal vibration. The values of p_1 can then be used in obtaining an accurate expression for the potential energy as a function of the volume. Such calculations are in progress.

I wish to thank Professor R. S. Krishnan for his interest in this investigation.

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[2] Kane, J. Chem. Phys. 7, 603 (1939).
[3] Walther, Haschkowsky, and Stvelkow, Physik. Zeits. d. Sowjetunion 12, 35 (1937).
[4] Gruneisen, *Handbuch der Physik*, Vol. X.
[5] Hunter and Seigel, Phys Rev. 61, 84 (1942).
[6] Huggins and Mayer, J. Chem. Phys. 1, 643 (1933)

Ultrasonic Velocity of Sound at 12 Mc in Liquid Sulfur

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July 26, 1950

IN other communications[1,2] the author has reported the application of the pulse-circuit technique to measure the ultrasonic velocity of sound in liquid metals The present communication refers to the application of the same technique for the measurement of the velocity of sound in liquid sulfur. Over a period of about four days a total of 29 separate measurements at temperatures from 115° to 315°C was carried out on a sample of liquid sulfur prepared from "Sulfur Sublimed, U.S.P. XII" (Mallinckrodt). The results of these measurements are plotted in Fig. 1. The data recorded in Table I were obtained from the smooth curve drawn through the experimental points.

It will be seen that there is no simple linear relationship between sound velocity and temperature. In fact, it appears that the curve in Fig. 1 has an inflection point in the transition region 160°–220°C, where the maximum viscosity is found. It should be pointed out that it was never possible to detect any hysteresis in the measured values for sound velocity during heating or cooling through this region.

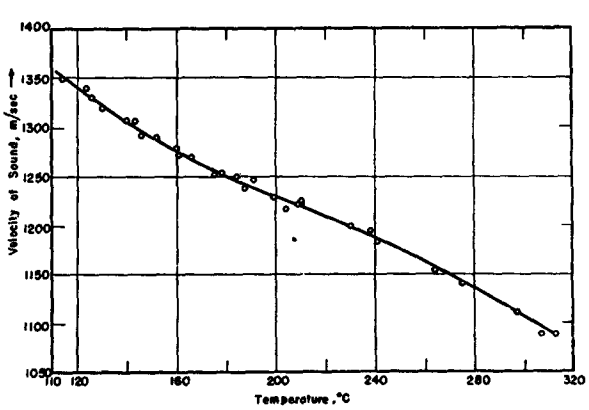

FIG. 1. Sound velocity as function of temperature.

TABLE I. Velocities of sound in liquid sulfur

Temperature, °C	Sound velocity (m/sec.)
115	135_0
150	129_0
200	123_0
250	117_5
300	110_5

Adiabatic and isothermal compressibility of liquid sulfur:—International Critical Tables' report for the density of liquid sulfur at 115°C, $\rho = 1.808$ g cm^{-3}, for the specific heat, $C_P = 7.27$ cal deg.$^{-1}$ and for the coefficient of thermal expansion, $\alpha = 4.3 \times 10^{-4}$ deg.$^{-1}$. Making use of these data we compute for liquid sulfur at 115°C:

Adiabatic compressibility, $K_S = 30.4 \times 10^{-6}$ bar^{-1}
Isothermal compressibility, $K_T = 34.6 \times 10^{-6}$ bar^{-1}.

Thus, $C_P/C_V = 1.14$ and specific heat, $C_V = 6.3_8$ cal. deg.$^{-1}$. The compressibility data may be compared with the isothermal compressibility of orthorhombic sulfur at 20°, which by I.C.T. is reported to be 13.1×10^{-6} bar^{-1}. The data thus indicate a very large increase in compressibility on fusion compared to what is found in the case of metals. These, in general, show an increase on fusion of about 15 percent only, while the same figure for sulfur appears to be of the order of 100 percent or more.

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Proton Magnetic Resonance in Polyethylene

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June 23, 1950

IN the course of some studies of the proton magnetic resonance in high polymers, a line-width transition was observed in polyethylene. Figure 1 summarizes the results. Figure 1a shows the line shape of the resonance at −186° and 25°C. Figure 1b shows the line width[1] as a function of temperature. As can be seen from the figure the midpoint of the line-width transition lies at about −38°C.

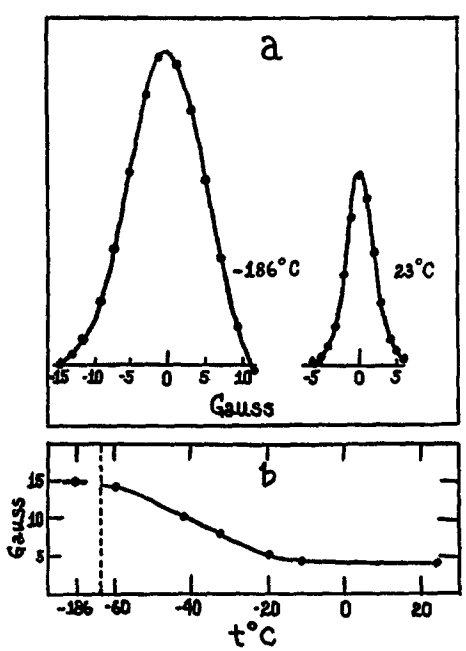

FIG. 1. Line shape data for polyethylene

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