The Effect of an Electric Field on the Thermal Conductivity of Glass

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of which is given in terms of valency-deformation and interaction forces. If l_i and θ_i are the bond lengths and angles, it may be written

$$2U = f_1 \sum \langle \Delta l_i^2 \rangle_{Av} + f_2 \sum \Delta l_i \Delta l_j + g_2 l^2 \sum \langle \Delta \theta_{ij}^2 \rangle_{Av} + g_4 l^2 \sum \Delta \theta_{ij} \Delta \theta_{ik} + g_5 l \sum \Delta l_i \Delta \theta_{jk} + g_6 l \sum [\Delta \theta_{ij} + \Delta \theta_{ik}] \Delta l_i.$$

Δl_i and $\Delta \theta_{ij}$ are respectively the changes of the NH and AsH bond lengths and of the H—N—H and H—As—H angles from their equilibrium position. The determinantal equation corresponding to that potential gives relations which have been computed by de Hemptinne and Delfosse.[4] On the assumption that the potential is the same in the hydrogenated and deuterated compounds, the force constants in the potential can be calculated with the harmonic frequencies. From these, if we use for the dimensions of the molecules the values given by Dennison[3] and McConaghie and Nielsen,[3] we obtain $f_1 = 7.171$; $f_2 = 0.074$; $g_2 = 0.612$; $g_4 = -0.087$; $g_5 = 0.291$; $g_6 = 0.436$ for NH$_3$ and $f_1 = 2.878$; $f_2 = -0.032$; $g_2 = 0.301$; $g_4 = -0.018$; $g_5 = -0.276$; $g_6 = 0.305$ for AsH$_3$. Every constant is expressed in units 10 dynes/cm.

Both series of figures show some striking features. The magnitude of the cross terms is not at all negligible as compared with valency forces, in spite of the fact that we are dealing with hydrogenated bonds. Among these forces, however, the length-length cross term f_2 is small, whereas the length-angle cross term g_6 is rather large. It may be worth while noticing that the relative smallness of f_2 seems a general property of hydrogenated bonds (CH$_4$, C$_2$H$_4$, H$_2$O, NH$_3$, AsH$_3$). As the cross terms measure the influence on one bond of a change in another bond or angle, they certainly arise from the hydrogen-hydrogen interactions and from the changes of hybridization at the central atom.[5] One of the main points is concerned with the change of the sign of f_2 in NH$_3(+)$ and AsH$_3(-)$. This fact presumably depends upon the influence of hybridization which plays a greater part in the former than in the latter. So the positive contribution of hybridization to f_2 would offset the negative contribution due to the H—H interactions in NH$_3$. Moreover, we have new evidence that the repulsive atom-atom interaction, which is the main factor in AsH$_3$, gives rise to a negative sign. Consequently, for molecules without resonance[5] and especially in case of hydrogenated bonds, the length-length cross term is expected to be negative (H$_2$O, H$_2$S, HCN, C$_2$H$_2$, AsH$_3$). It may however occur that the cross term becomes positive either by an offsetting due to hybridization of the central atom in favorable conditions (NH$_3$) or because the representative point of the atom-atom interaction is at the bottom of the atom-atom potential curve. The type of potential recently proposed by Duchesne and Monfils[1] is strongly supported by these results. A full account of this work will appear elsewhere.

[1] J. Duchesne and A. Monfils, J. Chem. Phys. 17, 586 (1949).
[2] J. W. Linnett and F. M. Hoare, Trans. Faraday Soc. 45, 844 (1949).
[3] D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940); V. M. McConaghie and H. H. Nielsen, Phys. Rev. 75, 633 (1949).
[4] M. de Hemptinne and J. M. Delfosse, Ann. Soc. Sci. Brux. 56, 373 (1936).
[5] Coulson, Duchesne, and Manneback, V. Henri Mém. Vol., Desoer, Liège (1948).

Molecular Structure of Methylbromosilanes

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MONOMETHYLTRIBROMOSILANE and dimethyldibromosilane were prepared by passing methyl bromide over heated silicon containing copper at 350°C.[1] Trimethylmono-

bromosilane was prepared by passing a mixture of methyl bromide and dimethyldibromosilane over heated aluminum at 350°C.[2]

The molecular structures of these compounds revealed by electron diffraction experiments at 20–30°C are summarized in Table I. Assumptions made at the calculation are (1) C—H distance 1.09A, (2) angle HCSi 109° 28' and (3) staggered relative position of Br and H in CH$_3$.

TABLE I.*

Compound	Number of rings observed	Si—Br	Si—C	BrSiBr	CSiBr
SiBr$_4$[a]	—	2.15±0.02A	—	109° 28'	—
CH$_3$SiBr$_3$	12	2.17±0.02	x	109° 28'	x
(CH$_3$)$_2$SiBr$_2$	11	2.21±0.03	1.92±0.06A	109° 28'	x
(CH$_3$)$_3$SiBr	9	2.21±0.03	1.86±0.05	—	105° ±4°

* x means undetermined.
[a] Spitzer, Howell, and Schomaker, J. Am. Chem. Soc. 64, 62 (1942).

The Si—Br distance is shorter than the sum of the covalent radii of Si and Br, that is 2.31A.[3] The observed Si—Br distance increases with the substitution of Br by CH$_3$ and this means the decrease of double bond character of Si—Br bond. The same phenomena were observed in the case of silicon tetrachloride and methylchlorosilanes where the following Si—Cl distances were observed: SiCl$_4$[4] 2.01±0.02A, CH$_3$SiCl$_3$[5] 2.01±0.02A, (CH$_3$)$_2$SiCl$_2$[5] 1.99±0.03A, (CH$_3$)$_3$SiCl[6] 2.09±0.03A.

[1] F. G. Rochow, J. Am. Chem. Soc. 67, 963 (1945).
[2] D. T. Hurd, J. Am. Chem. Soc. 67, 1545 (1945).
[3] L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1940), p. 164.
[4] Yamasaki, Kotera, Tatematsu, and Yokoi, J. Chem. Soc. (Japan) 69, 104 (1948).
[5] L. O. Brockway and R. L. Livingston, J. Am. Chem. Soc. 66, 94 (1944).
[6] R. L. Livingston and L. O. Brockway, J. Am. Chem. Soc. 68, 719 (1946).

The Effect of an Electric Field on the Thermal Conductivity of Glass

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WE have recently observed a phenomenon which is apparently little known and which may be of both theoretical and experimental interest. The effect observed is an increase in the thermal conductivity of glass when a high potential gradient is applied across it.

The experimental setup was made as follows: A pyrex insulator ring $\frac{3}{16}''$ long, $\frac{1}{4}''$ O.D., and with $\frac{1}{16}''$ wall thickness was clamped between two blocks of metal. The ends of the ring were highly polished as were the mating metal surfaces. One block of metal was maintained approximately at room temperature, while the other was heated to approximately 250°C by a tungsten heater. The assembly was operated in a vacuum of about 10^{-6} mm Hg. Roughly $\frac{3}{4}$ of the heat supplied to the heated block was conducted through the glass ring, the remainder being lost by radiation and by conduction through the electrical leads. The temperature of the heated block was measured with a thermocouple.

With constant heater power, the following effects were observed:

(1) Application of 3000 volts d.c. between the two blocks, with the heated block positive, caused a reduction in temperature of about 10°C, corresponding to a 4 percent increase in thermal conductivity.

(2) With reversed polarity, i.e., the heated block negative, no effect was observed.

(3) Using fused quartz in place of Pyrex, no effect was observed.

(4) Using Vycor, about half the effect noted with Pyrex was observed.

(5) Using a Pyrex ring with one face relieved a few thousandths of an inch except for three small projections, no effect was observed when the projections were in contact with the heated block; however, the effect was not reduced when the projections were in contact with the cold block.

In all cases, the leakage current was of the order of one microampere. It is possible that if more sensitive measuring apparatus had been employed some correlation of the effect with the leakage current would have been noticed.

The fact that the effect is polarity sensitive and that it depends on the contact area on the heated side suggests perhaps that it is related to the electrolytic action known to take place in glass. Since our efforts were aimed primarily at eliminating the effect in an existing piece of apparatus, rather than studying the effect *per se*, it is probable that more refined experiments would shed more light on the matter.

The Infra-Red Spectra of Liquid and Solid Methane*

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THE infra-red absorption spectra of liquid and solid methane in the rock salt region have been obtained recently in this laboratory using the Perkin-Elmer Model 12-B infra-red spectrometer. The purpose of this note is to describe these spectra briefly and to point out some of their more interesting features.

These spectra have been obtained at sample thicknesses of 12, 4, 0.4, and 0.1 mm in both the liquid and the solid. At the thickest of these sample layers the spectrum of the liquid consists simply of two regions which are completely absorbing, one from 1190 to 1825 cm^{-1}, and one from 2520 to 3340 cm^{-1}. By using progressively thinner sample layers, these regions are resolved into relatively broad peaks at 2600, 2820 and 3015 cm^{-1}, and an even broader peak at 1300 cm^{-1}, this last peak having a small shoulder at 1500 cm^{-1}. The spectrum of the solid presents absorption maxima at the same positions as those observed in the liquid, but the small shoulder appearing on the 1500 cm^{-1} band seems to be somewhat diminished. However, it is difficult to obtain quantitative information in this region due to the interference of the atmospheric water vapor spectrum. These spectra were obtained at various temperatures ranging from 77°K to 100°K. All these frequencies may be correlated with absorption frequencies previously observed in the gas.

Of particular interest is the shoulder at 1500 cm^{-1}, which apparently corresponds to the "optically inactive" fundamental ν_2 which has only very recently been observed in the infra-red spectrum of the gas.[1] The weak activity of this mode in the infra-red absorption spectrum of the gas is due to a Coriolis interaction of ν_2 with the optically active fundamental ν_4. This mechanism may also be partially operative in the condensed phases, but the transition may also be allowed, particularly in the liquid, as a result of the disturbance of the strict tetrahedral symmetry of the molecule by neighboring molecules.

These spectra were obtained with a variable-thickness transmission-type infra-red absorption cell and cryostat designed and constructed as a part of the low temperature spectroscopy program of this laboratory. Detailed descriptions of this apparatus and of the above reported spectra will be presented at a later date.

[1] John S. Burgess, Phys. Rev. **76**, 302 (1949).

The Kinetics of Heterogeneous Atom and Radical Reactions. II. The Recombination of Hydroxyl Radicals

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IN a recent paper (Part I)[1] we have applied the theory of absolute reaction rates to the calculation of surface recombination coefficients, and have arrived at probable mechanisms for the combination of hydrogen atoms on various types of surfaces and under different temperature conditions. It is the purpose of the present note to extend this treatment to the recombination of hydroxyl radicals.

It was found by Taylor and Lavin[2] that on a surface poisoned by water vapor the concentration of hydroxyl radicals decreases more rapidly than that of hydrogen atoms; assuming the disappearance to be on the surface, this would imply that the recombination coefficient for the OH radical, γ_{OH}, is greater than γ_H. Smith[3] made a more quantitative study, using glass and oxide surfaces poisoned by water vapor. At 453°K he found that γ was apparently 2.1×10^{-3}, which is less than for hydrogen atoms on clean glass by a factor of only about 10. However, the activation energy for the OH recombination was found by Smith to be $\sim$9 kcal., as compared with $\sim$1 kcal. for the hydrogen atom reaction. These facts would indicate a much higher frequency factor for the hydroxyl radical reactions, a result that is inconsistent with the fact that there is a loss of rotational and vibrational freedom in forming the activated complex.

This inconsistency becomes more apparent when quantitative calculations are made. Postulating the recombination mechanism to be either

$$S-OH+OH \rightarrow S+H_2O_2$$

or

$$S-OH+OH \rightarrow S-O+H_2O$$
$$S-O+H \rightarrow S-OH$$
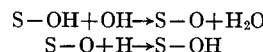
(by analogy with the mechanism of hydrogen atom recombination) the recombination coefficient is

$$\gamma = \frac{c_s h^2}{2\pi m k T b_g} \exp(-E/RT) \qquad (1)$$

(cf. Eq. (10), reference 1) where b_g, if the vibrational contribution is neglected, is equal to $8\pi^2 IkT/h^2$. Numerical evaluation for OH radicals using $c_s = 10^{15}$ gives $\gamma = (48.5/T^2)\exp(-E/RT)$; at 453°K and with $E=9$ kcal., one obtains $\gamma = 1.9 \times 10^{-7}$. This is less by a factor of 10^4 than the experimental figure, and agreement could only be obtained if in the calculation a zero activation energy were assumed. It may be noted that no heterogeneous mechanism will give a higher value of γ than the one above, as long as the activation energy of 9 kcal. is used.

In view of the good agreement found for hydrogen atom recombination, this discrepancy makes it extremely likely that the reaction investigated by Smith was not predominantly heterogeneous but occurred largely in the gas phase. Owing to experimental difficulties, Smith could not establish directly whether a surface or gas-phase reaction was more important; he considered the alternatives of surface recombination and homogeneous three-body reaction, and assumed the greater importance of the former because of the low pressure at which he worked. However hydroxyl radicals may also disappear by second-order gas-phase reactions, and a very probable one in this connection is

$$OH+H_2 \rightarrow H_2O+H.$$