

The Time Effect in the Fracture of Glass and Other Materials

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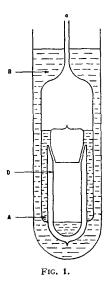
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The experimental arrangement is illustrated in Fig. 1. The vessel B represents the main helium bath. Immersed in B is the vessel A, of which a small Dewar, D, formed an integral part. The top of D was closed off by an evacuated glass plug ground to fit the Dewar. Atmospheric helium⁵ could be condensed in A, via the tube a. It was found that at 4.2°K the flow of helium through the ground joint at the top of D was negligible, even though the level of the liquid in A was well above the ground joint. From estimates of this minute flow, the channel width of the ground joint was assessed at 1 micron.

When the whole arrangement was cooled below the lambda-point, the liquid flowed rapidly from A into D, at 1.5°K the rate being 1.25 cc per minute, until the level in A fell just below the rim of the ground joint. From then on liquid would have flowed into D through the supra-surface film at a rate of approximately 10^{-2} cc per minute. The liquid remaining in A was evaporated at this stage, and subsequently the liquid in D was evaporated and its vapor collected separately.

The abundance ratio of helium isotope He³ in the vapor collected during two different runs was kindly measured for us by Professor Alfred O. Nier and Mr. L. T. Aldrich² to whom we wish to express our appreciation of their cooperation. The He³/He⁴ ratio for A was 1.85×10^{-6} and 1.55×10^{-6} for the two runs, this increase over the normal concentration for atmospheric helium² depending on the initial volume condensed. For the vapor from B the average values were 0.37×10^{-6} and 0.35×10^{-6} .

One may conclude that the He3 was at least partially filtered out by flow through the channel. It was difficult to estimate how complete this filtration might have been since in cooling from 4.2°K some liquid was condensed from the vapor already present in D. Calculation of this effect indicates that the filtration was almost complete, and certainly much more effective than might be concluded from direct calculation from the figures given above. Experiments to determine this effect more exactly are being persued and will be given in detail elsewhere.

The method of filtration of the isotope He³ by superfluid flow in the liquid phase, whether through supra-surface films3 or through narrow channels in the bulk liquid, is one which, apart from its theoretical interest, 4,3 may lead to an isolation of the rare isotope in sufficient quantities for many applications. Such work is now in progress.

* This work was assisted by Navy Contract No. N6onr-225.T.O.III between the Office of Naval Research and The Ohio State Research

Foundation.

¹ L. W. Alvarez and R. Cornog, Phys. Rev. 56, 379, 613 (1939).

² L. T. Aldrich and A. O. Nier, Phys. Rev. 70, 983 (1946); see also H. A. Fairbank, C. T. Lane, L. T. Aldrich, and A. O. Nier, Phys. Rev. 71, 911 (1947).

³ J. G. Daunt, R. E. Probst, H. L. Johnston, L. T. Aldrich, and A. O. Nier, Phys. Rev. 72, 502 (1947).

⁴ J. Franck, Phys. Rev. 70, 561 (1946).

⁵ We are grateful to Linde Air Products for kindly providing large quantities of atmospheric helium.

The Time Effect in the Fracture of Glass and Other Materials

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NE of the important problems in the mechanical properties of glass as well as of other substances is that of the delayed time to fracture. Specimens which do not fail during the time it takes a load to build up to its maximum value may subsequently fracture under the steady application of the load even in the absence of the chemical effects of the atmosphere, which will be the case considered here.

Considerable data have been accumulated and a variety of methods of plotting functions of fracture stress against functions of time have been advanced in the hope that one of them would yield a straight-line relationship and thereby disclose some rational explanation of the phenomenon. Most of the methods of plotting seem to show about equally good approximations to a straight line. This may be because of the experimental errors involved as well as the limited extent of the data.

The author proposes to treat the problem from the point of view of chemical-reaction rate theory in which the breaking of bonds between ions or atoms is the product of the reaction. Although this method has been used before,1 no account has been taken of either the rate at which the external loads are applied or of the effect of the breaking of bonds upon the remaining ones. The present treatment is an attempt to take both cases into account.

In the usual notation,2 the net number of jumps of the flow unit per unit time (rate at which bonds are broken) in the presence of a potential gradient is given by:

$$\frac{dN}{dt} = \frac{2kT}{h}e - \frac{\Delta F^*}{RT} \sinh \frac{w}{kT},\tag{1}$$

where N is the number of bonds broken and w is the work done per flow unit in the process. The latter may be related to the force, f, necessary to break a bond through $w = f(\lambda/2)$, where λ is some distance through which f must act to break the bond.

Equation (1) may be written:

$$dN/dt = A \sinh Bf, \tag{2}$$

where A and B do not depend upon the applied potential gradient.

If the load acts in a steady manner, it may be assumed as a first approximation that the force tending to break a bond increases directly with the number of bonds which have already been broken. Consequently, $f=f_0+cN$, where f_0 is the force tending to break the bond when the load is first applied. Substituting this relation into Eq. (2), integrating, and assuming that when fracture takes place the number of bonds broken is large, there results

$$f_0 = D \log \coth Et \tag{3}$$

as the relation between the initially applied stress, f_0 , and the time to fracture, t; D and E are constants which may be expressed in terms of A, B, and c. Through A and B the temperature dependence of the process may be studied.

For long times, Eq. (3) may be written:

$$f_0 = 2De^{-2Et}. (4)$$

For short breaking times, the effect of the rate of loading is predominant, and the additional stresses in the remaining bonds due to the breaking of bonds may be neglected. Assuming that the rate of loading is constant, f may be expressed in the form

$$f = rt. (4)$$

Substituting this into Eq. (2) and integrating leads to

$$t = (1/Br) \cosh^{-1} [(BrN_B/A) + 1],$$

 N_B being the number of bonds broken to bring about fracture. If the rate of loading is high and the first term in the parentheses large, this becomes approximately

$$t = (0/Br)\log Fr,\tag{5}$$

where F is a constant. This is a relation between the time to fracture, t, and the rate of loading, r. It is interesting to note that Eq. (5) also implies the temperature dependency of the process through the constant B and through F, which in turn depends on A and B. In a paper which the author expects to publish soon, the details and a comparison with experimental data will be given.

* Consultant to Glass Science, Incorporated.

1 E. S. Machlin and A. S. Nowick, N.A.C.A. Tech. Note No. 1126
(September, 1946).

(September, 1946).

² Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

A Formula to Detect Association in Liquids

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July 28, 1947

THERE are various formulas in literature which distinguish a normal liquid from an abnormal or associated liquid. In the following we present another such theory.

For normal liquids

$$E_X/V\alpha = T$$
,

and for associated liquids,

$$E_X/V_{\alpha} > T$$

in which E is cohesive energy in ergs per mole, expressed as the latent heat of vaporization minus RT, and written positive.

 χ is the isothermal compressibility in absolute units (barye⁻¹),

V is the molar volume in ccms,

 α is the coefficient of cubical expansion, and

T is the absolute temperature.

As an example, we compute the formulas at $20^{\circ}\text{C} = 293^{\circ}\text{A}$. (See Table I.) The data for the liquids were mainly taken

TABLE I. E_X/V_{α} for liquids.

| | | $\underset{\times}{E}$ | ~ | | | E_X |
|-----------------------------------------|-----------------------------------------|------------------------|---------------------------|----------------|---------------------|------------|
| No. | Liquid | ergs | $\times^{\chi}_{10^{12}}$ | V | α | $V\alpha$ |
| *************************************** | 34 | Class | I | | | |
| 1 | Pentane | 27000 | 200 | 114.9 | .001589 | 295 |
| $\tilde{2}$ | Iso-pentane | 25920 | 225 | 117.0 | .001533 | 325 |
| 2 3 4 5 6 7 8 9 | Hexane | 31390 | 150 | 130.3 | .001445 | 250 |
| 4 | Heptane | 35000 | 134 | 146.3 | .00115 | 279 |
| Ş | Octane | 37620 | 121 | 162.4 | .001124 | 249 |
| 7 | Decane Ether | 48280 27010 | 102 200 | 194.3 104 | .000988 | 256 310 |
| ģ | Acetone | 32016 | 100 | 73.5 | .001030 | 292 |
| g | Cyclohexane | 31080 | 109 | 105.4 | .00114 | 282 |
| 10 | Cyclohexanol | 50000 | 55 | 105.5 | .000804 | 324 |
| 11 | Carbon tetrachloride | 32953 | 105 | 96.5 | .001206 | 297 |
| 12 | Chloroform | 30989 | 100 | 80.2 | .001254 | 308 |
| 13 | Carbon disulphide | 28138 | 75 | 60.3 | .0011823 | 296 |
| 14 | Ethylene chloride | 33810 | 80 | 78.9 | .00112 | 308 |
| 15 16 | Ethylene bromide Methyl iodide | 42255 39110 | 60 56 | 86.1 62.2 | .000942 | 312 276 |
| 17 | Methyl acetate | 33670 | 90 | 79 | .001273 | 281 |
| 18 | Ethyl bromide | 29403 | 105 | 74.6 | .00141 | 293 |
| 19 | Ethyl iodide | 31980 | 95 | 80.8 | .001179 | 310 |
| 20 | Ethyl formate | 35558 | 75 | 80.2 | .001378 | 241 |
| 21 | Ethyl acetate | 34359 | 113 | 97.9 | .001359 | 292 |
| 22 | Ethyl propionate | 40800 | 98 | 115.0 | .001344 | 264 |
| 23 | Ethyl <i>n</i> -butyrate | 46440 | 95 | 132.2 | .001156 | 289 |
| 24 | n-Propyl acetate | 42840 33883 | 100 92 | 115.1 89 | .001214 | 306 282 |
| 25 26 | Benzene Aniline | 31080 | 92 44 | 89 84 | .000855 | 265 |
| 27 | Nitrobenzene | 43970 | 54.5 | 105 | .0008263 | 276 |
| 28 | Chlorobenzene | 42750 | 75 | 101.7 | .0009967 | 316 |
| 29 | Bromobenzene | 58090 | 50 | 105 | .00091505 | 302 |
| 30 | O-Xylene | 39220 | 75 | 118 | .000973 | 257 |
| 31 | m-Xylene | 38160 | 85 | 122 | .001009 | 274 |
| 32 | p-Xylene | 37600 | 80 | 124 | .001011 | 240 |
| 33 34 | Toluene | 35420 46200 | 92 50 | 106.3 112.2 | .001099 .0008681 | 279 259 |
| | p-Toluidine | | | 112.2 | .0000001 | 239 |
| | *************************************** | Class | | | | |
| 1 | Methyl alcohol | 37440 | 95 | 140 | .001229 | 735 |
| 2 | Ethyl alcohol | 41860 | 90 | 98 75 | .000739 | 520 533 |
| 4 | n-Propyl alcohol | 42600 41400 | 90 100 | 75 75 | .000956 .001094 | 493 |
| - 4 <u>-</u> | i-Propyl alcohol n-Buty! alcohol | 46620 | 99 | 91.4 | .001094 | 488 |
| 5 | i-Butyl alcohol | 45880 | 93 | 103.6 | .0009 | 458 |
| 7 | n-Amyl alcohol | 47520 | 85 | 110 | .000907 | 403 |
| 8 | Allyl alcohol | 40600 | 80 | 70 | .0001241 | 500 |
| 9 | Glycol | 50840 | 34 | 56 | .0006375 | 484 |
| 10 | Glycerine | 924000 | 22 | 73 | .000505 | 552 |
| 11 | Formic acid | 28520 | 55 | 37.7 | .000999 | 416 |
| 12 | Acetic acid | 27600 | 98 | 56 108.8 | .001065 | 454 453 |
| 13 14 | n-Valeric acid Mercury | 54129 5897934 | 90 3.4 | 108.8 | .0009886 | 453 745 |
| 15 | Water | 41706 | 45.5 | 18.06 | .00018109 | 5010 |

from International Critical Tables and tables of Landolt-Bornstein. Generally, a direct value of E and χ at 20°C and one atmospheric pressure was not available, and a rough reduction was made simply by guessing. The absence of round figures in most of the E values does not indicate the order of accuracy attained, but that the reduction was made for a value per g and then the value was multiplied