Studies on Glass XIV. Note on the Compressibility of Glucose Glass

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the absolute values of the velocities when compared for a given temperature and pressure are in agreement. Thus, the value of the quarter-life in the ethylamine decomposition at 482°C and 258 mm is 33 minutes which would correspond to a velocity constant of 1.5×10^{-4} sec.$^{-1}$. Now 258 mm of ethylamine would yield on the basis of the proposed mechanism 129 mm of diethylhydrazine. The velocity constant of 129 mm of the hydrazine at 510°C is 5.0×10^{-4} sec.$^{-1}$ which using an energy of activation of 39,000 calories gives at 482°C a value of 2.0×10^{-4} sec.$^{-1}$. Considering the approximate nature of the value based on the quarter-life this is in good agreement. It seems certain therefore that the control reaction in the ethylamine decomposition is the decomposition of diethylhydrazine.

In conclusion, it has been established that the decomposition of ethylamine proceeds by a bimolecular reaction yielding symmetrical diethylhydrazine and hydrogen followed by a subsequent decomposition of the hydrazine by a chain mechanism which overall is of first order. The former reaction is considerably more rapid than the latter and would be expected therefore to have a smaller energy of activation and smaller temperature coefficient. As the temperature is raised in the ethylamine decomposition therefore, the increase in the rate of the hydrazine decomposition will be relatively more rapid than the rate of its formation and the length of the induction period will decrease. The data given at 500°C show this to be the case, wherein the induction period is very short. One would anticipate that at 520°C the decomposition of ethylamine would show no apparent induction even at pressures as low as 50 mm. The original investigation by Taylor covered the temperature range 500 to 540°C and pressures from 50 to 400 mm, in other words was on the border line at which the induction period becomes appreciable. It is probable, however, that its complete nonobservance was due in part to the presence of traces of air in the system since the absolute rates there found are about twice as rapid as those herein quoted. The energy of activation 43,400 calories found in the earlier investigation is not considerably in error, lying in the range here found and indicates that there are no real discrepancies between the results found in both cases. The only discrepancy lies in the former interpretation of the observed results.

Studies on Glass
XIV. Note on the Compressibility of Glucose Glass

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The coefficient of cubical compressibility of glucose glass at 24°C has been found to be 18.8 (10^{-6}) atmos.$^{-1}$ for the pressure range 7–25 atmos. The relatively large intermolecular forces in polyhydroxy substances, such as glassy glucose and liquid glycerol, are indicated by a comparison of the compressibility and expansion coefficients for these and other typical organic compounds.

A VALUE for the coefficient of isothermal compressibility of glucose glass

$$[\beta = (-1/V)(\Delta V/\Delta P)_T]$$

has been needed in connection with some of the studies on glass which are being carried on in this laboratory. It is true that Cowper and Tammann[1] previously measured this coefficient for "amorphous" glucose and obtained a mean result of 12 (10^{-6}) atmos.$^{-1}$ at 20° for the pressure interval 240–1940 atmos. However, the present requirement was for a reliable value at con-

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[1] A. D. Cowper and G. Tammann, Zeits. f. physik. Chemie **68**, 281 (1909).

siderably lower pressures. Moreover, the technique of preparing clear glucose glass, free from bubbles, has been developed to a high degree in recent years here at Stanford. These considerations led us to the present determination.

After some preliminary experimentation the method developed and used extensively by Richards and his students[2] was adopted. A glass piezometer, closely following in details those described by Richards, was employed with mercury as the piezometric fluid around the sample of glucose glass. During the measurements it was placed within a strong steel bomb; various pressures, as desired, were then applied to this system from a cylinder of compressed nitrogen and were measured on a special test gauge.[3] The piezometer and bomb were kept at 24° in a carefully controlled thermostat.

The glucose glass samples were prepared by melting Pfanstiehl C. P. α-glucose crystals, heating the resulting liquid under a vacuum for ten or fifteen minutes at 170°C to eliminate air bubbles, then at atmospheric pressure pouring the material into small cylindrical molds made out of copper foil, and cooling these slowly down to room temperature in a desiccator. Full preparative details have been given in other places.[4] The small cylinders of annealed glucose glass thus obtained were carefully inspected for the inclusion of bubbles or other imperfections before use in the piezometer.

Two series of determinations on different samples of glucose glass yielded 18.2 and 19.4 (10^{-6}) atmos.$^{-1}$, respectively, for β in the pressure interval 7–25 atmos. Thus our mean result (probably accurate to within 5 percent) is 18.8 (10^{-6}) atmos.$^{-1}$ at 24°. This temperature is approximately in the middle of the "transition

TABLE I. *Some compressibility and expansion coefficients.* (At 20°C unless otherwise indicated.)

SUBSTANCE	β (10^6 atmos.$^{-1}$)	α (10^4 degree^{-1})
Ethyl alcohol (liquid)	111.3	10.8
n-Heptane (liquid)	142.4	12.2
Benzene (liquid)	94.9	12.1
Benzene (crystalline)	34.1 (0°)	—
Glycerol (liquid)	24.0	4.8
Glucose (glassy)	18.8 (24°)	1.4

region"[5] in which many of the properties of carefully prepared samples of glucose glass change rather rapidly in magnitude.

It is interesting to compare this compressibility value with those for a few other typical organic compounds. We have done this in Table I, where the values for β for liquid ethyl alcohol, *n*-heptane, benzene and glycerol have been calculated from the sonic measurements of Freyer, Hubbard and Andrews.[6] They refer to 20° and 1 atmos. pressure. The value for crystalline benzene has been derived by extrapolation of the data of Richards, Bartlett and Hodges[7] and refers to 0°C and 1 atmos. pressure. As both the coefficients of compressibility (β) and of thermal expansion $[\alpha = (1/V)(\Delta V/\Delta T)_P]$ serve as rough measures of the magnitude of the intermolecular forces in a material, we have also tabulated values[8] for the latter at 20° in the last column of the table. From these data it is evident that the intermolecular forces in polyhydroxy compounds, such as liquid glycerol and glassy glucose, must be considerably greater than in ordinary liquids or even in a typical nonpolar crystal, such as crystalline benzene. Such a situation is undoubtedly a very favorable factor in the formation of a stable glass.

[2] T. W. Richards, W. N. Stull, J. H. Matthews and C. L. Speyers, J. Am. Chem. Soc. **34**, 971 (1912); T. W. Richards and E. P. R. Saerens, ibid. **46**, 934 (1924).

[3] Professor U. A. Patchett of the Department of Mechanical Engineering kindly calibrated this gauge for us.

[4] G. S. Parks, H. M. Huffman and F. R. Cattoir, J. Phys. Chem. **32**, 1366 (1928); G. S. Parks, L. E. Barton, M. E. Spaght and J. W. Richardson, Physics **5**, 193 (1934).

[5] G. S. Parks, S. B. Thomas and D. H. Light, J. Chem. Phys. **4**, 64 (1936).

[6] E. B. Freyer, J. C. Hubbard and D. H. Andrews, J. Am. Chem. Soc. **51**, 759 (1929).

[7] T. W. Richards, E. P. Bartlett and J. H. Hodges, J. Am. Chem. Soc. **43**, 1538 (1921).

[8] The sources of these α values are: *ethyl alcohol and benzene*, reference 6; *n-heptane*, G. Edgar and G. Calingaert, J. Am. Chem. Soc. **51**, 1540 (1929); *glycerol*, J. W. Lawrie, *Glycerol and the Glycols* (The Chemical Catalog Co., New York City, 1928), pp. 155–165; *glucose glass*, L. J. Snyder, Master's Thesis, Stanford University (1929).