The Decomposition of Ethylamine and Diethylhydrazine

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The decomposition of ethylamine has been reinvestigated in the light of criticism of earlier work. The reaction has been shown to occur by a bimolecular no volume change decomposition into symmetrical diethylhydrazine and hydrogen followed by the decomposition of the hydrazine by a chain mechanism which is first order. The mechanism is shown to account for the induction period and its rapid variation with temperature and pressure, as well as accounting satisfactorily for apparent discrepancies and inconsistencies found by previous workers.

IN a previous study of the decomposition of ethylamine[1] it was found that the course the reaction followed was apparently homogeneous and unimolecular. As a result of further work on dimethylamine[2] doubt was cast on this seeming simplicity of reaction as "probably fortuitous due to a mutual compensation of several reactions." Later in the same year Schumacher and Wiig[3] published the results of an investigation of the ethylamine decomposition at lower pressures and concluded that the reaction was heterogeneous and complex, probably involving a chain mechanism. This latter conclusion was drawn from the erratic nature of the decomposition, the effect of added gases notably water vapor and air, the effect of a change in surface and from the reaction products which were found to be mainly hydrogen, methane and nitrogen, with small amounts of unsaturated hydrocarbons and some basic material. This tremendous divergence of observation alone would call for further study. Schumacher offers no explanation. Unfortunately the evidence presented is not consistent as indicated by his inability to reproduce a temperature coefficient. Sickman and Rice[4] also conclude from a study of the decomposition of propylamine at low pressures that the reaction probably has a chain mechanism though again no detailed mechanism is offered.

The fundamental point of difference between this later work and the earlier work by Taylor appears to lie in the existence of an induction period, never observed by him, found by Sickman and Rice only at lower pressures (5 mm) and by Schumacher and Wiig especially at lower temperatures and lower pressures but markedly erratic, showing little consistency or reproducibility.

The presence of an induction period caused by an initial acceleration of the rate of a reaction has so frequently been regarded, either as an annoying complication in an otherwise apparently simple reaction and hence to be disregarded as innocuously as possible for subsequent quantitative treatment, or gratuitously, as an indication of the presence of a chain mechanism, that it was deemed advisable to study this case in more detail in an endeavor to reconcile the conflicting results mentioned. Although it has not been found possible to elucidate the mechanism completely, numerous observations have been made, which, pointing to the same conclusions, leave no doubt as to the main steps involved and offer an explanation of the apparent inconsistencies so far observed.

The mechanism postulated is, for the main part, the following:

$$2C_2H_5NH_2 \rightarrow C_2H_5NH-NHC_2H_5 + H_2$$
$$C_2H_5NH-NHC_2H_5 \rightarrow N_2 + H_2 + 2C_2H_5.$$
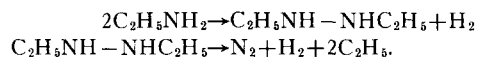
It seems advisable to justify this scheme qualitatively before discussing the quantitative results. In the first place, on allowing ethylamine vapor at pressures from 400 to 500 mm, to remain at 300°C, some 200° below the temperature at which a noticeable pressure increase occurs, a pressure decrease was observed. This was traced to the condensation in the capillaries joining the reaction vessel and manometer, of

[1] H. Austin Taylor, J. Phys. Chem. **34**, 2761 (1930).
[2] H. Austin Taylor, J. Phys. Chem. **36**, 1960 (1932).
[3] H. J. Schumacher and E. O. Wiig, Zeits. f. physik. Chemie **A162**, 419 (1932).
[4] D. V. Sickman and O. K. Rice, J. Am. Chem. Soc. **57**, 22 (1935).

some higher boiling material formed in the early stages of reaction. The condensation was completely eliminated by heating the capillaries to 85°C under which circumstances no pressure change was noted even after several days. The occurrence of a reaction at so low a temperature precluded the possibility of the condensate being a polymer of an unsaturated hydrocarbon as a product of the decomposition proper and the significance of the temperature necessary to prevent condensation is apparent since the boiling point of symmetrical diethylhydrazine is given as 84° to 86°C.

Analyses of the gases in the reaction system at the end of the induction period showed a large excess of hydrogen over the nitrogen and hydrocarbon and several times the percentage of hydrogen found by Schumacher in the final products of decomposition. Taken in conjunction with the above-mentioned evidence for a reaction at low temperature involving no change in volume, this elimination of hydrogen necessitates the first step postulated. To prove definitely the presence of diethylhydrazine samples of liquid products were condensed in dynamic decompositions of ethylamine which showed fractions boiling at 84° to 86°C. This liquid had reducing properties, showing easy reduction of ammoniacal silver nitrate and difficult reduction of Fehling's solution, properties characteristic of the hydrazine. Samples of liquid ethylamine sealed in bomb tubes and heated at 300°C for a period of a few hours likewise showed the same product. In fact it was found possible to produce a relatively pure sample of the hydrazine by allowing ethylamine vapor to circulate rapidly through a small furnace at 250° to 300° in a closed system. The furnace temperature as well as the time of contact is sufficiently low that subsequent decomposition of the hydrazine is reduced to a minimum and the extent of reaction may be judged by the hydrogen pressure developed. Fig. 1 illustrates a convenient form of the apparatus.

In the hope of obtaining kinetic measurements of this, the primary reaction, samples of ethylamine vapor sealed in small tubes were heated at 400°C in a lead bath for various lengths of time and titrated with iodine to determine the amounts of diethylhydrazine produced. The re-
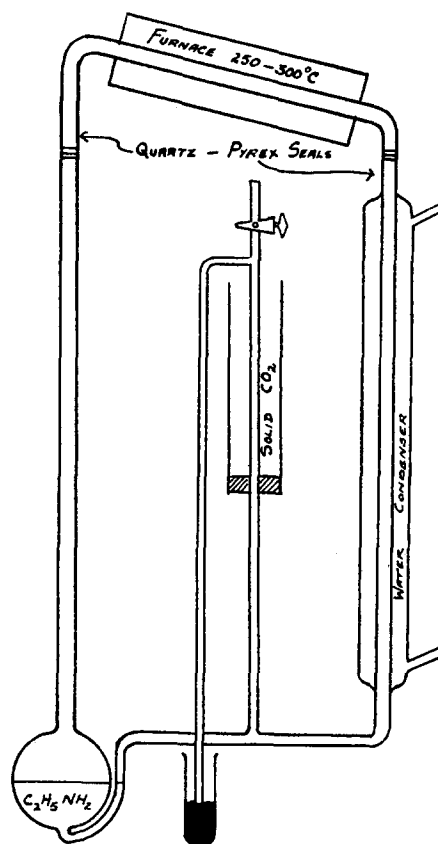
FIG. 1. Apparatus for production of diethylhydrazine from ethylamine.

sults showed a qualitative increase in concentration of the hydrazine with time of heating but quantitatively were not consistent. This was traced by titrations of known samples of amine and hydrazine to an indefiniteness in the endpoint of the iodine titration, apparently a function of the amine content.

With the foregoing results as complete evidence of the first stage of ethylamine decomposition, the fact that it involves no change in the number of molecules would be responsible for an induction period in a rate measurement in terms of pressure change. That it alone is responsible was shown by a separate study of the decomposition of diethylhydrazine. This latter proceeds at measurable speed in the temperature range 500° to 540°C, the same as that for ethylamine and under no circumstances was found to give an induction period. However, if air or oxygen had been in contact with the hydrazine

previous to its admission to the reaction flask, or if air was present even in very small amounts in the reaction flask upon admitting the hydrazine, the decomposition was immeasurably rapid at 500° and could only be measured conveniently around 300°C. This phenomenon is readily explicable by the easy oxidation of the hydrazines to the corresponding azo compounds.[5] There is no reason to believe that azoethane would differ greatly from azomethane in its decomposition and should therefore decompose easily around 300°C to yield nitrogen and ethyl radicals. A sample of diethylhydrazine containing a small amount of air would therefore resemble a system undergoing decomposition induced by ethyl radicals at the temperature necessary merely to produce the radicals thermally. Once contamination by air had been observed as indicated by the fast decomposition, it was found only necessary to freeze the diethylhydrazine in solid carbon dioxide and evacuate the system thoroughly, after which the normal rate of decomposition at the higher temperatures again obtained.

The decomposition of diethylhydrazine must therefore be a chain reaction and for that reason the second equation given above in the mechanism postulated has been left in terms of ethyl radicals. Were these to combine to give butane the over-all reaction would be

$$C_2H_5NH - NHC_2H_5 \rightarrow N_2 + H_2 + C_4H_{10}$$
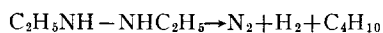
corresponding to a 200 percent pressure increase. Actually as is shown later butane is found but naturally under the conditions of the experiments in quite small amounts. The reactions of free ethyl radicals either alone or in presence of free hydrogen have been well studied[6] and lead to the expectation of finding methane as the principal product with more or less unsaturated hydrocarbon in a polymerized form depending on the amount of hydrogen present. The pressure increase observed for the complete reaction of decomposition of either ethylamine or diethyl-

hydrazine is consistent with this view. What the individual steps in the hydrazine chains are cannot be specified. Suffice that the over-all reaction is of first order but shows a variation with pressure that has come to be associated with a chain mechanism and a variation with temperature that is not strictly of the Arrhenius type. Further discussion is deferred until the observed data have been presented.

EXPERIMENTAL

The rates of decomposition of ethylamine and diethylhydrazine were measured by following the rate of pressure change manometrically. The reaction vessel was of fused quartz, the rest of the apparatus being Pyrex. Evacuation was obtained through a Langmuir mercury vapor pump backed by an oil pump, although samples could also be drawn off the system by means of a Töpler pump. The connecting capillaries between reaction vessel and manometer were heated to 90°C in all experiments for the reason stated above.

Since earlier work had indicated the necessity of using highly purified materials special care was taken in this regard. The purification of ethylamine is a very difficult task with the result that many commercial samples on the market labeled pure may contain as much as 2 percent ammonia as well as secondary amine. This was true of the Eastman Kodak sample which was the starting material. The purification followed the method of Pohland and Mehl[7] being virtually a fractional distillation in vacuum between the temperatures of solid carbon dioxide and solid carbon disulphide. The vapor pressure of the purified product measured at 0.4°C was 273 mm in agreement with their values.

The diethylhydrazine was prepared by the Thiele[8] method adapted for the ethyl derivative in place of the methyl in the original. Diformylhydrazine is ethylated with diethylsulphate and then hydrolized with concentrated hydrochloric acid. The hydrazine is distilled from an alkaline solution and repeatedly fractionated from barium oxide until dry.

[5] No mention of azoethane is found in the literature. It seems highly probable that this is due to the easy oxidation of the diethylhydrazine. Chromic acid which is satisfactory for the methyl derivative causes complete destructive oxidation of the ethyl compound and azoethane can only be produced by use of a very mild oxidizing agent.

[6] H. S. Taylor and D. G. Hill, J. Am. Chem. Soc. 51, 2922 (1929).

[7] E. Pohland and W. Mehl, Zeits. f. physik. Chemie A164, 48 (1933).

[8] Thiele, Ber. 42, 2576 (1909).

TABLE I.

TEMPERATURE 482°C				TEMPERATURE 490°C						TEMPERATURE 500°C			
INITIAL PRESSURE (mm) TIME (min.)	224.5	258	299	INITIAL PRESSURE (mm) TIME (min.) 33	37.5	58	69	105		INITIAL PRESSURE (mm) TIME (min.) 79.5	89	107	123
	PRESSURE INCREASE (mm)				PRESSURE INCREASE (mm)						PRESSURE INCREASE (mm)		
2	0.5	0.5	1.0	4	—	0.5	0.5	1.5	4.0	1	1.0	1.0	1.0	2.5
5	2.0	2.5	3.0	6	—	1.0	1.5	2.5	7.0	2	2.5	2.5	3.5	8.0
10	4.5	5.5	8.0	8	0.5	1.5	2.0	4.0	10.0	3	4.0	4.0	7.0	13.0
20	10.0	13.0	20.5	10	1.5	2.5	3.0	5.5	13.5	4	5.5	7.0	10.0	18.0
30	19.5	24.0	35.0	12	2.0	3.5	4.5	7.5	17.0	5	7.5	9.0	13.5	22.5
40	33.0	39.0	57.0	14	2.5	4.0	6.0	10.0	21.0	10	17.5	21.5	30.0	46.5
50	46.5	55.0	81.0	16	3.0	5.0	7.0	12.5	24.5	20	38.0	46.5	60.0	85.0
60	62.0	73.0	103.0	18	4.0	6.0	8.5	15.5	28.5	30	53.5	65.0	83.0	106.0
70	79.0	92.0	127.0	20	4.5	7.0	10.0	18.5	32.5	40	64.0	74.5	100.5	121.0
80	93.0	109.0	149.5	25	7.0	10.0	14.5	26.0	42.5	50	70.5	82.0	114.5	131.5
90	109.0	126.0	167.5	30	9.0	12.5	19.0	32.0	51.0	60	75.5	87.5	124.0	138.5
100	124.0	143.0	186.5	35	11.5	15.0	23.0	36.5	59.0					
110	136.5	157.0	203.5	40	14.0	18.0	27.0	40.5	66.0					
130	160.0	184.0	229.5	50	18.5	23.0	33.0	46.0	78.0					
150	179.0	205.0	248.0	60	22.0	27.0	37.0	49.5	87.5					
180	201.5	231.0	270.0											

RESULTS AND DISCUSSION

Ethylamine

The point of prime importance in the case of ethylamine is the complete reproducibility with relative ease of the reaction rate, including the induction period, when due care is taken in the use of pure material with the exclusion particularly of all traces of oxygen. It was at one time suspected during the course of the work, that reaction products strongly adsorbed on the reaction vessel walls were responsible for some observed inconsistencies which were only removed after at least twelve hours pumping. This was finally traced to a poorly fitting stopcock allowing an access of air to the ethylamine reservoir. This corrected, reproducible results were obtainable after a comparatively short evacuation of one or two hours at 10^{-4} to 10^{-5} mm.

Since interest centered on the induction period static runs were made at 482°, 490° and 500°C at pressures from 25 to 300 mm. The pressure increase at the endpoint was fairly consistent ranging generally between 125 and 130 percent. A few cases where the value was as low as 100 percent seem exceptional, though all the values are of little importance since they depend so much on the hydrocarbon equilibrium obtaining in the secondary reactions. Actual values of the pressure increase at corresponding times are given in Table I for the three temperatures

studied and initial ethylamine pressures indicated. Fig. 2 illustrates the results at 490° and shows qualitatively the variation of the induction period with pressure.

Kontorova and Neumann[9] and more recently Semenoff[10] have attempted to account theoretically for the auto-accelerating rates of numerous reactions, the former on the basis of the formation of a specific intermediate, the latter by chain reactions. In the former treatment it is concluded that the formation of an intermediate without a volume change followed by its decomposition with a volume change will not give an induction period of measurable duration, when the order of the two reactions is the same. It is not proved that if the reactions are of different order the same conclusion holds. It is obvious that if the order of the two reactions is the same the ratio of the rates alone need be considered, whilst if the orders are different, the initial concentration as well as the ratio of rates must be taken into account. Semenoff finds that in numerous cases an auto-accelerating rate may be expressed by a logarithmic relation, similar to that used by Garner[11] and his co-workers in the decomposition of solid explosives, which appears suggestive of a chain reaction. The application to the data herein

[9] T. A. Kontorova and M. B. Neumann, Physik. Zeits. Sowjetunion 4, 818 (1933).
[10] N. N. Semenoff, Acta Physiocochim. U. R. S. S. 1, 113 (1934).
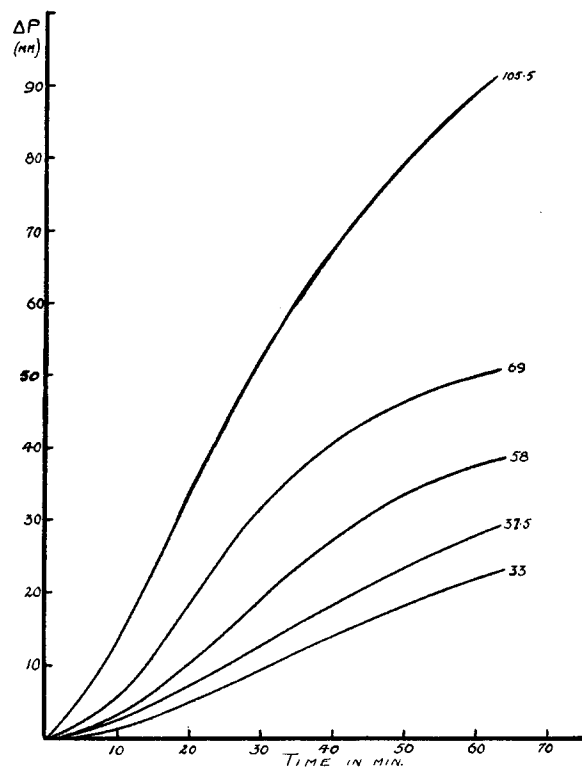[11] Garner, J. Chem. Soc. 1393 (1933).

FIG. 2. Rates of pressure change of ethylamine at 490°C.

proves of little value and need not be given, especially since in any case, it could not be used as proof that the induction period has its origin in a chain mechanism.

On the other hand if the mechanism of the ethylamine reaction here postulated is correct, at least an approximate idea of the order of the initial reaction may be obtained from the limiting slope of the plot of pressure change against time, at zero time. The order is found to be two as shown by the constancy of the values obtained by dividing the limiting slope by the square of the initial concentration. The values are expressed in concentration units of moles per liter and time in seconds in Table II.

TABLE II.

TEMPERATURE 482°C		TEMPERATURE 490°C	
INITIAL PRESSURE	$k \times 10^3$	INITIAL PRESSURE	$k \times 10^2$
224.5	2.96	33	2.20
258	3.33	37.5	2.25
299	3.16	58	1.90
		69	3.33
		105	4.50

The constancy of these values is all that may be expected in view of the inevitable error in taking slopes at zero time which is precisely that region of the reaction where experimental determinations are most difficult. It is for this reason that similar values are not given for the data at 500°C where the induction period is very short and hence the curvature of the rate curve is very great. That the values may not be used to calculate a temperature coefficient for the first reaction is obvious since the very existence of a slope signifies that a pressure increase, that is the second reaction, has already occurred to a small extent. The conclusion is inescapable however, that the formation of diethylhydrazine is of second order.

According to the proposed mechanism, at the point of inflection of the curve of the pressure change against time the rate of production of the hydrazine is equal to its rate of decomposition. Since the formation is shown to be the more rapid reaction this means that the ethylamine concentration will have become negligible at this point and hence the rest of the curve may be treated as corresponding solely to the hydrazine decomposition. Taking the point of inflection as the origin of the remainder of the curve the fractional life of the final reaction may be estimated for the various temperatures and pressures studied. These data are presented in Table III as the time in minutes for one-quarter

TABLE III.

TEMPERATURE 482°C INITIAL PRESSURE	$t_{1/4}$	TEMPERATURE 490°C INITIAL PRESSURE	$t_{1/4}$	TEMPERATURE 500°C INITIAL PRESSURE	$t_{1/4}$
224.5	35	33	15	79.5	14
		37.5	15	89	13
258	33	58	13	107	12
		69	10		
299	29	105	15	123	8

of the total pressure change.

The values show a marked decrease with increase of pressure, a variation frequently found in chain reactions, but not so great as would be expected for a bimolecular reaction. The reaction appears to be much more nearly first than second order. Unfortunately the pressure ranges studied at the three temperatures do not overlap so that an accurate determination of the energy of

activation from the temperature coefficient at some constant pressure cannot be made. However by plotting the logarithms of the reciprocal times, that is a quantity proportional to the velocity constant, against the logarithm of the pressure the curves may be extrapolated, assuming they are parallel over a short pressure range and hence an approximate temperature coefficient at a fixed pressure determined. The average value so found for the energy of activation is 38,000 calories. These values will be referred to later for comparison with the results on the hydrazine alone.

The results of the analyses of the products of decomposition at the end of the induction period, mentioned in the introduction are given in Table IV. Ethylamine at pressures of 600 and

TABLE IV.

	(1)	PERCENT (2)
Hydrogen	48.25	54.87
Methane	36.83	29.16
Butane	5.26	4.17
Unsaturated	3.51	8.33
Nitrogen	6.14	3.47

650 mm was allowed to decompose at 490°C until the pressure had increased by from 15 to 25 percent.

The products were then withdrawn by means of a Töpler pump, washed with acid to remove basic material including any unchanged amine and hydrazine and the resulting gases analyzed, the butane being frozen out. The high percentage of hydrogen is striking especially if compared with the 10 percent found by Schumacher and Wiig in the final products. The amount of nitrogen is surprisingly low in view of the amount of methane. The only available explanation appears to lie in the possibility that most of the nitrogen corresponding to this methane as a product of the diethylhydrazine already decomposed at the end of the induction period, was still present as basic material and hence removed in the preliminary washing. It is well known that hydrazine itself may decompose giving either nitrogen and ammonia alone or nitrogen, hydrogen and ammonia. It may well be then that diethylhydrazine would yield ammonia or amines on partial decomposition. Schumacher finds a

small amount of basic material even in the final products and in view of the probable chain mechanism of the hydrazine decomposition the presence of the nitrogen entirely as free nitrogen should not be expected.

Diethylhydrazine

The decomposition of the hydrazine itself was studied at temperatures from 510° to 540°C. The reaction proceeded without an induction period and was approximately unimolecular during a given run. The endpoint of the reaction varied between 100 and 110 percent pressure increase. The magnitude of the velocity constants calculated by the usual first-order equation for the various observations made in a given experiment show a decided falling trend. The constants quoted therefore are the extrapolated values from the limiting slope of the pressure change-time curve at zero time divided by the initial pressure. Table V gives a resumé of the results obtained.

TABLE V.

INITIAL PRESS. (mm)	TEMPERATURE (°C)	$k \times 10^4$ sec.$^{-1}$	INITIAL PRESS. (mm)	TEMPERATURE (°C)	$k \times 10^4$ sec.$^{-1}$
263	510	5.5	165	530	8.8
164	510	5.1	52	530	8.0
161	510	4.9	32	530	7.3
241	520	7.5	254	540	17.3
143	520	6.5	245	540	17.2
53	520	5.9	150	540	12.5
32	520	5.7	62	540	10.0
238	530	11.7	29	540	9.3

The general shape of these curves is similar to that found for the corresponding curves of quarter-life calculated from the later portions of the ethylamine reaction. They appear to show a divergence at higher pressures which would indicate a varying energy of activation with pressure, a condition not uncommon in chain reactions. The average energy of activation calculated by the Arrhenius equation from the velocity constants at a fixed pressure around 250 mm is 45,000 calories, whilst at 150 mm is 39,000 calories. This latter value is to be compared with the 38,000 calories found from the quarter-lives of the later portions of the ethylamine decompositions averaged around the same pressure as previously indicated. Furthermore

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).