Contributed Original Research

Pressure and Temperature Effects on the Viscosity of Liquids*

DAVID FRISCH AND HENRY EYRING
Frick Chemistry Laboratory, Princeton University, Princeton, New Jersey

AND

JOHN F. KINCAID
Department of Chemistry, University of Rochester, Rochester, New York

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The free energy of activation for viscous flow is related to an entropy and energy of activation by the same equations as any equilibrium. This, for the theory of viscosity is perfectly general and independent of the mechanism. The rolling over each other of pairs of molecules lying in adjoining layers is the mechanism which appears to be the most probable, and the equations for this bimolecular flow process are developed here. At low pressures the heat of activation for viscous flow is about one-third the energy of vaporization, but as the pressure is raised, it increases rapidly because of the work term, PV/n'. Here P is the external pressure, V is molal volume and V/n' is the extra volume required before the flow process can take place. Calculations made for n-pentane, ether, benzene, iso-pentane, water, and mercury over as extended a temperature and pressure range as the data permit are found to agree satisfactorily with the experimental viscosity. The results are interpreted in terms of the liquid structure and the mechanism of viscous flow. The results of applying our theory to the liquids for which the necessary data is available show that the effect of pressure on viscosity can be calculated *a priori*, with thermodynamic data only, with reasonable success.

THE general equation for the rate of any process in which matter rearranges by surmounting a potential energy barrier has been proposed in the following form:[1-3]

$$k' = \kappa (F^*/F_n)(\bar{p}/m^*),\qquad(1)$$

where F^* is the partition function for the activated complex per unit length normal to the potential barrier, $\bar{p}$ is the corresponding average momentum, and m^* is the reduced mass. F_n is the partition function for the normal state; κ is the transmission coefficient, the chance that a system having once crossed the potential barrier will react and not recross in the reverse direction. Eq. (1) states that the absolute rate of a reaction is the product of the number of molecules per unit length in phase space at the top of the barrier by the velocity at the top of the barrier, multiplied by an efficiency factor.

We assume that there is no "tunneling" under the barrier, and that the activated complex has nearly all the properties of an ordinary molecule except that instead of having only the three regular translational degrees of freedom, it has a fourth, along which it approaches the barrier, crosses it, and flies to pieces. We can now write (F^*/F_n) as $(F^\ddagger/F_n)(2\pi\mu^* kT)^{\frac{1}{2}}/h \exp(-\Delta E_0/kT)$ where $F^\ddagger$ is the partition function of the activated complex without the fourth degree of translational freedom per unit length represented by $(2\pi\mu^* kT)^{\frac{1}{2}}1/h$, and ΔE_0 is the energy of activation. The usual expression for the average velocity in the forward direction across the barrier is:

$$(\bar{p}/\mu^*) = (kT/2\pi m^*)^{\frac{1}{2}}\qquad(2)$$

and Eq. (1) becomes

$$k' = \kappa(F^\ddagger/F_n)(2\pi m^* kT)^{\frac{1}{2}}/h$$
$$\times \exp(-\Delta E_0/kT)(kT/2\pi m^*)^{\frac{1}{2}}$$
$$= \kappa(F^\ddagger/F_n)kT/h \exp(-\Delta E_0/kT).\qquad(3)$$

Assuming $\kappa = 1$, this becomes

$$k' = (F^\ddagger/F_n)(kT/h)\exp(-\Delta E_0/kT).$$

We now review[4-6] briefly the application of this general theory of reaction rates to liquids and treat certain aspects more explicitly. The most probable mechanism of liquid flow is the rolling past each other to new equilibrium positions of pairs of molecules in adjoining layers; the frequent occurrence of this basic process shifts the layers of molecules and constitutes flow. This process is illustrated in Fig. 4 of Hirschfelder, Stevenson and Eyring.[7] The configuration in which the molecules are halfway by each other, having broken part of their bonds and having also accumulated the necessary extra space, constitutes the activated complex. The activation energy required for the passing of the molecules is the energy of activation of viscous flow, $\Delta E_{vis}(\equiv \Delta E_0)$.

The distance measured along the velocity gradient between two neighboring pairs of molecules sliding past each other is taken as λ_1. The average distance between equilibrium positions in the direction of motion is taken as λ while the distance between neighboring molecules in this same direction is λ_2, which may or may not equal λ. λ_3 indicates the molecule-to-molecule distance normal to the direction of motion and to λ_2 and λ_1. By definition we have for the viscosity $\eta = f\lambda_1/\Delta v$. Here f is the force per square centimeter tending to displace one layer with respect to the other, and Δv is the difference in velocity of these two layers which are at a distance λ_1 apart. The force acting on a single molecule is $f\lambda_2\lambda_3$, and it acts to lessen the work of passing over the barrier through a distance $\lambda/2$, so that in the forward direction the height of the barrier is in effect lowered by the amount $f\lambda_2\lambda_3\lambda/2$, while in the backward direction it is raised by the same amount. The number of times that a molecule moves in the forward direction in a second may be written as the corresponding specific reaction rate:

$$k_f = (F^\ddagger/F_n)kT/h$$
$$\times \exp\left[-(2\Delta E_0 - f\lambda_2\lambda_3\lambda)/2kT\right]. \quad (4)$$

For the backward direction:

$$k_b = (F^\ddagger/F_n)kT/h$$
$$\times \exp\left[-(2\Delta E_0 + \lambda_2\lambda_3\lambda)/2kT\right]. \quad (5)$$

[4] H. Eyring, J. Chem. Phys. 4, 283 (1936).
[5] R. H. Ewell and H. Eyring, J. Chem. Phys. 5, 726 (1937).
[6] H. M. Smallwood, J. App. Phys. 8, 505 (1937).
[7] Hirschfelder, Stevenson and Eyring, J. Chem. Phys. 5, 896 (1937).

Hence:

$$\Delta v = \lambda(k_f - k_b) \quad (6)$$
$$= \lambda(F^\ddagger/F_n)hT/h$$
$$\times \exp(-\Delta E_0/kT)\{\exp f\lambda_2\lambda_3/2kT$$
$$-\exp(-f\lambda_2\lambda_3\lambda/2kT)\}$$
$$= \lambda(F^\ddagger/F_n)kT/h$$
$$\times \exp(-\Delta E_0/kT)2\sinh(f\lambda_2\lambda_3\lambda/2kT)$$

and

$$\eta = f\lambda_1/\Delta v = f\lambda_1[\lambda(F^\ddagger/F_n)kT/h$$
$$\times \exp(-\Delta E_0/kT)2\sinh(f\lambda_2\lambda_3\lambda/2kT)]^{-1}. \quad (7)$$

Now for ordinary viscous flow $f\lambda_2\lambda_3\lambda \ll kT$, so that expanding the exponential and keeping the first power terms only we have after cancellation:

$$\eta = \lambda_1 kT[\lambda^2\lambda_2\lambda_3(F^\ddagger/F_n)kT/h$$
$$\times \exp(-\Delta E_0/kT)]^{-1} \quad (8)$$
$$= (\lambda_1 h/\lambda^2\lambda_2\lambda_3)(F_n/F^\ddagger)\exp(\Delta E_0/kT).$$

It is interesting to check the assumption $f\lambda_2\lambda_3\lambda \ll kT$. While Bridgman[8] does not give the exact data necessary to compute f, we can determine its order of magnitude. The annular space between the falling weight and the cylinder wall in his experiment was of the order of 10^{-2} cm. The weight fell at a velocity roughly of the order of 1 cm/sec. Viscosity is defined by the equation: $\eta = fd/\Delta v$ where d is the distance between the layers across which the velocity gradient Δv is measured.

$$f = \eta\Delta v/d \approx 10^{-2}/10^{-2} = 1 \text{ dyne/cm.}^2$$

Since
$$\lambda_2\lambda_3\lambda \approx V/N$$
$$f\lambda_2\lambda_3\lambda \approx 10^2/10^{23} = 10^{-21}$$
$$T \approx 300°K$$
$$k \approx 10^{-16} \text{ erg/deg./mole}$$
$$kT \approx 10^{-14}.$$

So we are justified by a factor 10^{-7} in assuming $f\lambda_2\lambda_3\lambda \ll kT$. We develop somewhat more fully than has been done previously the form of the general expression

$$k' = (F^\ddagger/F_n)kT/h \exp(-\Delta E_0/kT)$$

for the particular case of a bimolecular process. By bimolecular we mean that molecules one and two in two contiguous layers move simultane-

[8] P. M. Bridgman, The Physics of High Pressure (Macmillan Co., 1931).

ously in such coordinates of $x_2y_2z_2$, it is co three coordina pair

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[9] Kincaid and

ously in such a way as to pass each other. If the coordinates of molecule one are $x_1y_1z_1$ and of two $x_2y_2z_2$, it is convenient to replace these with the three coordinates of the center of gravity of the pair

$$X = (m_1x_1 + m_2x_2)/(m_1+m_2),$$
$$Y = (m_1y_1 + m_2y_2)/(m_1+m_2),$$
$$Z = (m_1z_1 + m_2z_2)/(m_1+m_2),$$

and the three components of the distance between the pair $x = x_2 - x_1$, $y = y_2 - y_1$, $z = z_2 - z_1$. Now if the direction of flow is in the x direction, the activated state will correspond to $x = 0$, and we can speak of x as the reaction coordinate. Using classical mechanics which is adequate for viscous flow in the cases with which we are here concerned, we obtain:

$$(F^{\ddagger}/F_n)(kT/h) = \delta q \int_0^{\infty} \exp(-p^2/2\mu^*kT)(p/\mu^*\delta q)dp \left[\int_{-\infty}^{+\infty} \exp(-p^2/2\mu^*kT) \int_0^{V_f^{\frac{1}{3}}} dx \right]^{-1}$$

$$= (kT/2\pi\mu^*)^{\frac{1}{2}} \cdot V_f^{-\frac{1}{3}} = (kT(m_1+m_2)/2\pi m_1 m_2)^{\frac{1}{2}} V_f^{-\frac{1}{3}}. \quad (9)$$

The arbitrary length, δq, along the reaction path normal to the top of the potential barrier is seen to cancel out of the final result. Here we have assumed that $F^{\ddagger}$ and F_n cancel for all degrees of freedom except the reaction coordinate. The reduced mass in the x direction is $\mu^* = m_1 m_2/(m_1+m_2)$. The limits 0 to $V_f^{\frac{1}{3}}$ for $x = x_1 - x_2$ in the above integral follow from the fact that configurations of the normal state for which $x_1 > x_2$, only, are to be considered.

This then gives us

$$F_n/F^{\ddagger} = (2\pi\mu^*kT)^{\frac{1}{2}} V_f^{\frac{1}{3}}/h, \quad (10)$$

where V_f is the free volume, defined as the total integral over that part of the potential energy which is due to thermal displacements of the center of gravity from its equilibrium position. Combining Eqs. (8) and (10) we have

$$\eta = \lambda_1/\lambda^2\lambda_2\lambda_3(2\pi\mu^*kT)^{\frac{1}{2}} V_f^{\frac{1}{3}} \exp(\Delta E_{\mathrm{visc}}/kT). \quad (11)$$

If λ is equal to λ_1,

$$\lambda_1/\lambda^2\lambda_2\lambda_3 = N/V \quad (12)$$

and we have

$$\eta = (\pi RMT)^{\frac{1}{2}}/V(V_f^{\frac{1}{3}}/N^{\frac{1}{3}}) \exp(\Delta E_{\mathrm{visc}}/RT), \quad (13)$$

in which all units are now molar. Since we have assumed the process bimolecular, we have written $N\mu^* = (N(m_1m_2/m_1+m_2) = M/2$.

Kincaid and Eyring[9] develop the equation $V_f^{\frac{1}{3}} = (u_g/u_1)V_1^{\frac{1}{3}}$ where u_g is the velocity of sound in the gas and u_1 the velocity of sound in the liquid. Substituting we get

[9] Kincaid and Eyring, J. Chem. Phys. **6**, 620 (1938).

$$\eta = (\pi RMT)^{\frac{1}{2}} N^{-\frac{1}{3}}(u_g/u_1 V_1^{\frac{2}{3}})$$
$$\times \exp(\Delta E_{\mathrm{visc}}/RT). \quad (14)$$

Both velocities may be evaluated by the hydrodynamic formula $u = (v/\beta_s)^{\frac{1}{2}}$ where v is the specific volume and β_s the adiabatic compressibility. This becomes $u_g = (\gamma RT/M)^{\frac{1}{2}}$ for an ideal gas, where γ is the ratio of specific heat at constant pressure to that at constant volume.

We must now evaluate ΔE_{visc}, the energy of activation for viscous flow. This energy is required to adjust the surroundings of a pair of molecules so that they can pass each other. At comparatively low pressures all that is needed is that some fraction of the bonds between two adjacent molecules and their neighbors be broken or stretched enough so that this pair can pass by each other. The energy of activation for viscous flow at low pressures turns out to be about $\frac{1}{4}$ the energy of vaporization. Our equation now becomes

$$\eta = (\pi RMT)^{\frac{1}{2}} N^{-\frac{1}{3}}(u_g/u_1 V_1^{\frac{2}{3}})$$
$$\times \exp(\Delta E_{\mathrm{vap}}/nRT), \quad (15)$$

where n is a constant lying between 3 and 5 for normal liquids. The fraction of bonds broken is a function of the type of molecule and the structure of the liquid. For any normal liquid the fraction of bonds broken will not vary with the temperature, i.e., n is a constant. Hence the empirical rule, $\eta = A \exp(B/T)$.

This evaluation of the activation energy for viscous flow holds at comparatively low pressures only, for only then can we neglect the work of expansion against the external pressure necessary

to make the hole in which the molecules pass each other. At high pressures we must add on to $\Delta E_{vap}/nRT$ the term $P\Delta V/RT$ where P is the external pressure and ΔV the volume of the hole formed against it. ΔV will be some fraction V/n' of the molecular volume, giving

$$\eta = (\pi RMT)^{\frac{1}{2}} N^{-\frac{1}{3}} (u_g/u_1) V_1^{-\frac{1}{3}}$$
$$\times \exp(\Delta E_{vap}/nRT + PV/n'RT). \quad (16)$$

n' will often vary over the experimental pressure range because as the liquid becomes compressed and the molecular volume decreases, a different fraction of the molecular volume is needed to give the same amount of space for the passing of molecules. Liquids such as water undergo structural changes under pressure that would naturally alter rapidly the free space available for molecular passage without making an additional hole, thus affecting n'.

Solids unlike liquids are not able to introduce a hole a fraction the size of a molecule without profoundly altering the crystal structure in the neighborhood of the molecules passing each other. This alteration in structure could take the form of a compression of neighboring molecules. In this case it can be estimated from the well-known thermodynamic expression for the free energy of compression. This way of obtaining the necessary cavity permitting viscous flow would be expected to be more extravagant of free energy than the method of over-all expansion possible in the comparatively structureless liquids. In fact in solids it may be cheaper from the free energy point of view to diffuse only where a molecule is omitted from the lattice than by distortion of a perfect lattice.

The procedure followed in the computations is to use the experimental viscosity, the energy of vaporization, the velocity of sound in both the liquid and the gas, and the other terms on the right-hand side of Eq. (15) to determine n, giving

TABLE I.

SUBSTANCE	n, E. AND E.	n (THIS PAPER)	n' (MEAN VALUE)	n'/n (THIS PAPER)	η(obs.) η (COMPUTED)
n-Pentane	3.5	4.4	7.8	1.8	1.1
Diethyl Ether		4.5	7.8	1.6	1.9
Benzene	2.6	3.3	5.5	1.7	0.6
Iso-Pentane		4.4	8	1.8	1.9
Mercury	20	11	23	2.1	2.8

the proper temperature variation of viscosit This is done over as wide a temperature range the data warrant and at atmospheric pressur employing the sound velocity data of Frey Hubbard and Andrews,[10] and other data fr Landolt-Bornstein Tabellen. The values of n o tained in this way, given in Table I, are th used in Eq. (16) in order to obtain values of at a given temperature and different pressure The viscosity and P-V-T data are those gi by Bridgman.[8] By the use of the P-V-T data, t energies of vaporization were in all cases correct to the particular pressure in question. A summa of the results for n' is given in Table II.

The values of n given in column three Table I lie in a slightly different range than tho of Ewell and Eyring[5] shown in column two cause a different evaluation of the free volur has been used here. Column six of Table shows that the value for n which gives the rig temperature coefficient of viscosity also gives t absolute value to within better than an averaj factor of 2 for liquids other than those class as "hydrogen-bonded."

TABLE II. *Values of n' as computed from the data at various pressures.*

PRES-SURE kg/cm²	n-PEN-TANE 30°C	DIETHYL ETHER 52.5°C	BEN-ZENE 25°C	ISO-PEN-TANE 50°C	MER-CURY 0°C	WATER 0°C
1,000	6.0		5.5	8		124
2,000	6.9	4.7			25.0	14
4,000	8.5	6.0			23.0	8
6,000	9.7	6.8			24.2	(5000)7.
8,000	10.4	7.2				
10,000	10.8	7.6				
12,000		7.9				

The individual computations of n' are sho in Table II. The treatments possible for benze and for iso-pentane warrant giving only o value for n'. It will be noted that n' for pentane, ether, and mercury does not va greatly over the entire experimental pressu range, but that n' for water ranges from 124 1000 kg/cm² to 7.2 at 5000 kg/cm² This var tion is interpreted as follows: at low pressu water has an open, four-coordinated structure

[10] Freyer, Hubbard and Andrews, J. Am. Chem. S 51, 759 (1929).
[11] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, (1933).

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and no extra volume is required for the activated complex for flow to form. As the pressure is increased, the open structure collapses, and at high pressures the activated complex needs as much extra space to form as is required by any other nonspherical molecule. It is probably incorrect to assume that n is constant for these liquids at one temperature and varying pressures, but the value of n' is not greatly affected by a considerable change in n. Table III illustrates

TABLE III. *Values of n' for water for different values of n at 0°C.*

P (kg/cm)	$n=2$	4	5.4
1,000		16.1	124
2,000	32	16	14
3,000	19	11	9.7
4,000	14	8.8	8.0
5,000	10.6	7.7	7.2

that the n' values computed for water using different n's converge to about the same limit at high pressures.

The fifth column of Table I gives the ratio of the mean value of n' over the pressure range to the value of n. The fact that this ratio is nearly constant and equal to 1.6–1.8 for the four non-metallic liquids in the table is of some significance. It has been previously shown[4] that the energy required to form a hole in a liquid the size of a molecule is equal to the energy of vaporization. Although it might be reasonable to assume a linear relationship between the size of the hole formed and the energy required to form it, the fact that the ratio, n'/n is not unity, but 1.75 indicates that this is not the case. Taking the data for ether as an example, we find an n' of 7, indicating that a hole approximately 1/7 the size of the molecule is required for viscous flow. However, the activation energy is 2/9 times the energy of vaporization. We accordingly have the interesting physical result that there is an energy of dissociation of large holes into smaller ones, i.e., two holes, each 1/7 the size of a molecule cost considerably more energy than one hole 2/7 molecular size. In case of ether, seven holes, each 1/7 the size of a molecule would liberate energy equal to 14/9 the energy of vaporization, on being combined into a single cavity of molecular dimensions.

The ratio n'/n for mercury does not differ greatly from that for the nonmetallic liquids in the Table, but n and n' are themselves much greater. This has been previously explained[5, 12] as being due to movement of the metallic ions in viscous flow, rather than of the atoms. That the ratio of n' to n is again approximately two for a hole as small as 1/23 the size of the atom is an interesting fact.

Figure 1 shows plots of observed and computed viscosities as a function of pressure for ether, mercury, and n-pentane, with constant values of n and n' in Eq. (16). The results of the present work lead us to suggest that viscosities under pressure may be computed with reasonable accuracy by Eqs. (15) and (16) by using only thermodynamic data and viscosity measurements at atmospheric pressure. For normal, non-metallic liquids n' for use in Eq. (16) is equal to 1.75 times the value of n from Eq. (15). For metallic liquids the factor (n'/n) may be somewhat higher but only one test case is available. Although it is impossible at present to *predict* the pressure effect on viscosity for liquids in which the molecules are bound by directional bonds
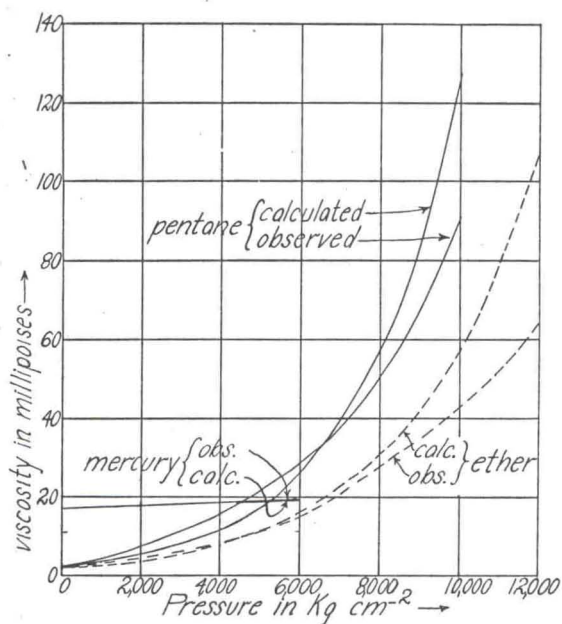

FIG. 1. Comparison of observed viscosities and those computed from Eq. (16). The values of n are 4.5, 12 and 4.4 of n' 8, 23 and 10 for ether, mercury and pentane, respectively.

[12] J. Kincaid and H. Eyring, J. Chem. Phys. 5, 588 (1937).

TABLE IV. *Summary of data used in the computations.*

Liquid	Pressure in kg/cm²	$(\partial E/\partial V)T$ in kg/cm²	E_{vap} kg/cm	Free Volume in cc/mole	Observed Viscosity in Milli-poises
n-Pentane	1	1,640	238,800	1.21	2.20
at 30°C	1,000	2,420	269,600	0.32	4.54
	2,000	2,310	283,050	.151	7.35
	3,000	2,110	291,010	.097	
	4,000	1,480	296,950	.068	15.5
	5,000	150	298,630	.053	
	6,000	−620	298,120	.044	28.5
	7,000	−1,240	296,520	.036	
	8,000	−1,090	294,850	.029	50.4
	9,000	−910	293,650	.023	
	10,000	−1,150	292,650	.020	90.7
Diethyl	1	2,190	227,500	1.52	1.83
Ether	1,000				
at 52.5°C	2,000	2,400	272,800	.128	5.46
	4,000	1,860	286,200	.071	10.50
	6,000	970	291,800	.048	17.58
	8,000	120	293,200	.034	27.75
	10,000	1,370	291,900	.028	42.69
	12,000	−2,050*	290,400	.023	64.24
Water	1	−162	435,500	0.439	17.92
at 0°C	1,000	+518	435,540	.292	16.50
	2,000	775	436,000	.204	17.15
	3,000	845	436,730	.149	18.35
	4,000	673	437,800	.114	19.91
	5,000	−112	438,900	.096	21.83
Mercury	1	12,675	599,800	0.0119	
at 0°C	2,000	12,186	601,100	.0114	
	4,000	12,355	602,100	.0109	
	6,000	12,928	602,900	.0105	

* At 11,000.

(e.g., water and alcohols), the method of computation employed here yields interesting information about the structure and the mechanism of viscous flow in such liquids.

In our calculation of viscosities we have treated the flow of individual molecules only and have neglected the fact that aggregates of molecules can flow as units also. More precisely to the calculated fluidity for the single mechanism we should add the fluidity due to the double, triple and higher multiple molecule mechanisms. That our approximation ordinarily neglects factors considerably smaller than two in the fluidity may be seen by comparing the theoretical or experimental fluidity of molecules with values for molecules twice as large but otherwise similar. This aspect of the subject will be developed in detail at a later time.

Appendix

Since the data used in making the computations are of some interest for their own sake, they are assembled in Table IV. The data for benzene and for iso-pentane have not been done in enough detail and are over too short a pressure range to justify their inclusion in this Table. The free volumes have been computed from sound velocities, and the thermodynamic data are from the data given by Bridgman.[8]

An X-Ray Study of Acetylsalicylic Acid When Incorporated in Certain Sugars

Ronald L. McFarlan and J. Wallace Reddie

Department of Research and Technology, United Drug Company, Boston, Massachusetts

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Introduction

CONFLICTING claims have recently been advanced regarding the possibility of incorporating acetylsalicylic acid—aspirin—into certain sugar bases as a solid solution. The original claims made regarding the existence of such a solid solution[1] have been subsequently denied[2] as a result of certain x-ray experiments. In these latter experiments only x-ray diffraction patterns consisting of a series of sharp lines—characteristic of a mixture of powdered crystalline fragments—are reported. Unpublished preliminary x-ray studies of this problem made in the summer of 1935 yielded a diffraction pattern for the sugar bases consisting of a single, broad diffuse ring—characteristic of an amorphous or glass-like material. Since the types of x-ray patterns obtained differ so sharply it has seemed worth while to examine once more the whole problem from an x-ray point of view.

Preparation of Samples

Sucrose and glucose were mixed with sufficient additional water to assure a complete solution of

[1] E. C. Merrill, Chem. Abs. **31**, 5949 (1937).
[2] S. S. Sidhu, J. App. Phys. **9**, 546 (1938).