

ULTRASONIC ANALYSIS OF MOLECULAR RELAXATION PROCESSES IN LIQUIDS

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Introduction.—Propagation of a sound wave through a liquid takes place adiabatically except at very high frequencies which are outside the range at present available experimentally. Thus as the pressure in the liquid alternates about the static or ambient pressure at a frequency $f (= \omega/2\pi)$, there will be a corresponding variation in the temperature at any point. If c is the phase velocity at a frequency f then the variations in excess of pressure in a plane progressive sound wave can be expressed by

$$p = p_0 \exp(-\alpha x) \exp[i\omega(t - x/c)]$$

where x is the distance measured in the direction of propagation, p_0 is the amplitude of the pressure variations at the source ($x = 0$) and α is the amplitude absorption coefficient of the liquid through which the wave is propagated.

This Review is concerned with the interpretation of absorption data for pure liquids and their binary mixtures. In the first place there is a contribution to the total absorption due to the shearing motion which occurs in the propagation of a plane wave: this is generally termed the "classical" absorption* and is expressed in terms of the shear viscosity, η , by

$$\left(\frac{\alpha}{f^2}\right)_{\text{classical}} = \frac{8\pi^2\eta}{3\rho c^3} \text{ (sec.}^2 \text{ cm.}^{-1}\text{)}$$

The quantity $(\alpha/f^2)_{\text{classical}}$ is independent of frequency for a particular liquid at a given temperature except in the case of highly viscous liquids in which the shear viscosity is frequency-dependent.¹

Other contributions to the absorption of sound waves in liquids arise from time-dependent molecular processes. Thus whenever the molecules can reside in two or more equilibrium states *which differ in energy* (although they may have the same volume) it is possible for this equilibrium to be perturbed by the sound wave. Consider for example the case of a first-order reaction $A_1 \rightleftharpoons A_2$ for which k_{12} , k_{21} are the appropriate rate constants. The important parameter as far as the sound wave is concerned is the relaxation time $\tau = (k_{12} + k_{21})^{-1}$. At sufficiently low frequencies ($\omega\tau \ll 1$)

¹ Litovitz *et al.*, *J. Acoust. Soc. Amer.*, 1951, **23**, 75; 1954, **26**, 566, 577.

* There is an additional contribution arising from the energy lost from the sound wave owing to thermal conduction but this is negligible, except in mercury and liquid helium.

the molecular distribution between states A_1 and A_2 follows the variations in the sound wave. On the other hand, at very high frequencies ($\omega\tau \gg 1$) the internal equilibrium is sensibly unaffected by the sound wave. As the frequency increases from a low value ($\omega\tau \ll 1$) there is an increasing phase retardation between the population of a given energy state and the excess of pressure of the sound wave. This is accompanied by a decrease in the magnitude of the changes in population density with the result that the absorption per unit of wavelength, μ ($= \alpha c/f$), passes through a maximum near a "characteristic frequency", $f_c = (k_{12} + k_{21})/2\pi$. There is an accompanying decrease in the quantity (α/f^2) from its low-frequency value to a limiting high-frequency value when $f \gg f_c$ (see Fig. 2). Such a behaviour is termed ultrasonic relaxation and, with certain approximations, can be represented by an equation of the form ²

$$\frac{\alpha}{f^2} = 1 + \frac{A}{(f/f_c)^2} + B$$

Here the term B represents the combined effects of absorption due to shear viscosity and any further relaxation processes having a characteristic frequency much greater than the value of f_c for the particular mechanism considered.

Measurements of the absorption of sound waves in liquids have revealed the existence of relaxation processes which can be given a molecular interpretation. Moreover, the detailed study of the behaviour at different temperatures, and over a frequency range sufficient to delineate a major part of the relaxation, enables the parameters of the reaction in question to be evaluated for processes which, in many cases, are not readily observable by other methods. From the chemical point of view the field of study can be termed the investigation of fast reactions. A particular feature of the ultrasonic method of observing such reactions is its sensitivity to very low population densities (of the order of 1 per cent. and less) in the higher-energy state.

Experimental results on which an analysis can be based have, in the main, originated in the past few years. The measuring techniques which have been developed are now used to an increasing extent by physical chemists, thus providing a further analytical method for the study of molecular behaviour which is complementary to the established techniques of infrared spectroscopy, dielectric absorption, etc. Simultaneously with experimental developments there has been corresponding progress in the theoretical understanding of relaxation processes based on the methods of irreversible thermodynamics.³ Familiarity with the theory is essential to the chemist who desires to correlate experimental results with molecular behaviour and the purpose of this Review is to present a summary both of the fundamental theory and of the outstanding experimental results with their molecular interpretation.

² Andreae and Lamb, *Proc. Phys. Soc.*, 1956, **69**, B, 814.

³ Meixner, *Ann. Physik*, 1943, **43**, 470; *Acoustica*, 1952, **2**, 101; Davies and Jones *Phil. Mag.*, 1953, **2** (Suppl.), 370; Davies, *Proc. Roy. Soc.*, 1954, *A*, **226**, 24.

The technique which provides the greatest accuracy in determining the absorption coefficient is the pulse method: ⁴ this is generally employed at frequencies above 5 to 10 Mc./sec. and accuracies of $\pm 2\%$ in (α/f^2) have been achieved up to frequencies as high as 200 Mc./sec.⁵

In the frequency range 1 to 10 Mc./sec. the method of acoustic streaming which has been recently developed ⁶ has considerable advantage over other measuring techniques, particularly for low-absorbing liquids: absorption measurements can be obtained to within $\pm 5\%$ accuracy.

A reverberation technique is employed at frequencies in the range 100 kc./sec. to 1 Mc./sec.⁷ but corrections which must be applied to the recorded results are mainly responsible for a relatively poor accuracy of measurement—*ca.* $\pm 15\%$ in (α/f^2) .

In connection with the experimental observation of relaxation processes it should be mentioned that an increase in the phase velocity takes place with increasing frequency over the relaxation region. It can readily be seen why, in general, it is more profitable to measure the absorption rather than the velocity for, if acetic acid at 25° C is taken as an example, the total change in velocity over the relaxation region is only 1.7% whilst the absorption falls from $(\alpha/f^2) = 132,000 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$ at low frequencies to $140 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$ at high frequencies—a factor of 1000.

A further point of importance is the extent of the frequency range required to delineate a relaxation. The relaxing part of (α/f^2) is expressed by $A/[1 + (f/f_c)^2]$ and this falls from 0.9A to 0.1A in one decade of frequency. In practice, a somewhat wider range of frequency is to be desired and this must, of course, be roughly centred about f_c in order to permit the results to be analysed satisfactorily.

The thermodynamic theory of relaxation and the propagation of sound

Static Thermodynamic Relations.—It is convenient to collect here some essential thermodynamic reasoning about a simple fluid system containing a single chemical reaction mechanism or, more generally, a single ordering process. It is clear that to define the state of such a system we require three independent variables. In the first instance we shall choose the temperature (T), the pressure (p), and an ordering parameter (z) which, in the case of a chemical reaction specified by the stoichiometric formula $\sum_i \nu_i M_i = 0$, can be taken as the degree of reaction. In this case, therefore, the change in mole number of the i -th constituent due to the reaction is given by $dN_i = \nu_i dz$. The dependent thermodynamic variables are the entropy (S) and the volume (V), conjugate respectively to T and p , and the affinity (A) conjugate to z . In the case of a chemical reaction we have

$$A = - \sum_i \nu_i \mu_i \quad . \quad . \quad . \quad . \quad (1)$$

⁴ Pinkerton, *Proc. Phys. Soc.*, 1949, **62**, B, 286.

⁵ Andraee, Heasell, and Lamb, *ibid.*, 1956, **69**, B, 625.

⁶ Piercy and Lamb, *Proc. Roy. Soc.*, 1954, A, **226**, 43; Piercy, *J. Phys. Radium*, 1956, **17**, 405.

⁷ Karpovich, *J. Acoust. Soc. Amer.*, 1954, **26**, 819.

and for all cases we assume the existence of a Gibbs function $G(T,p,z)$ such that for any change of state in the system :

$$-dG = SdT - Vdp + Adz \quad . \quad . \quad . \quad (2)$$

Thus $-A = (\partial G/\partial z)_{p,T}$ is the change in Gibbs function due to the "reaction" per unit change in z at constant T and p ; it is sometimes denoted by ΔG .

The first-order derivatives of the dependent variables S , V , and A are of three types :

(i) The *thermodynamic coefficients* $C_p \equiv T(\partial S/\partial T)_{p,z}$, $\alpha \equiv (1/V)(\partial V/\partial T)_{p,z}$, and $\kappa \equiv (-1/V)(\partial V/\partial p)_{T,z}$. It should be noticed that they are the heat capacity, expansivity, and compressibility of the system *taken at fixed z*. They are sometimes called the "frozen", "glassy", or "instantaneous" coefficients.

(ii) The *reaction coefficients* $\Delta S \equiv (\partial S/\partial z)_{p,T}$ and $\Delta V \equiv (\partial V/\partial z)_{p,T}$. For the chemical case we have $\Delta S = \sum_i \nu_i s_i$ and $\Delta V = \sum_i \nu_i v_i$ where s_i and v_i are partial molar quantities. ΔS and ΔV are the entropy and volume changes due to the reaction per unit change of z .

(iii) The *ordering coefficient* $\beta \equiv (\partial A/\partial z)_{p,T}$. This gives a measure of the curvature in the plot of G against z at constant T and p . For the case of a chemical reaction we have from equation (1) that

$$\beta = -\sum_i \sum_j \nu_i \nu_j (\partial \mu_i / \partial N_j)_{p,T} \quad . \quad . \quad . \quad (3)$$

The condition for thermodynamic equilibrium is that G should be a minimum for variations at constant p and T . This condition is therefore that

$$-\Delta G = A(p,T,z) = 0 \quad . \quad . \quad . \quad (4)$$

which relation fixes the equilibrium value of z as a function of T and p .

Variations in the dependent variables are given by the equations

$$\left. \begin{aligned} dS &= (C_p/T)dT - V\alpha dp + \Delta Sdz \\ dV &= V\alpha dT - V\kappa dp + \Delta Vdz \\ dA &= \Delta SdT - \Delta Vdp + \beta dz \end{aligned} \right\} \quad . \quad . \quad . \quad (5)$$

In the special case for which z is fixed we have of course the familiar relations

$$\left. \begin{aligned} (dS)_z &= (C_p/T)dT - V\alpha dp \\ (dV)_z &= V\alpha dT - V\kappa dp \end{aligned} \right\} \quad . \quad . \quad . \quad (6)$$

Consider now the case in which changes are made so slowly that z is allowed to attain its equilibrium value at each instant, that is, changes subject to $A = 0$ or $dA = 0$. Solving the last member of eqn. (5) for dz and substituting the result in the first two members, we then have

$$\left. \begin{aligned} (dS)_A &= [(C_p - T \Delta S^2/\beta)/T]dT - [V(\alpha - \Delta S \Delta V/\beta V)]dp \\ (dV)_A &= [V(\alpha - \Delta S \Delta V/\beta V)]dT - [V(\kappa - \Delta V^2/\beta V)]dp \end{aligned} \right\} \quad (7)$$

We now introduce a notation which distinguishes the "equilibrium" thermodynamic coefficients by means of a bar and denotes the difference between "equilibrium" and "frozen" coefficients by δ

$$\delta C_p \equiv \bar{C}_p - C_p \equiv T(\partial S/\partial T)_{p,A} - T(\partial S/\partial T)_{p,z}$$

Equation (7) can therefore be written in a form analogous to eqn. (6) :

$$\left. \begin{aligned} (dS)_A &= (\bar{C}_p/T)dT - V\bar{\alpha}dp \\ (dV)_A &= V\bar{\alpha}dT - V\bar{\kappa}dp \end{aligned} \right\} \quad . \quad . \quad . \quad (7')$$

and the "excess" or "difference" properties are given by

$$\left. \begin{aligned} \delta C_p &= -T \Delta S^2/\beta \\ \delta\alpha &= -\Delta S \Delta V/\beta V \\ \delta\kappa &= -\Delta V^2/\beta V \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (8)$$

This is an important result because it shows how the "excess" thermodynamic coefficients can be related to the reaction coefficients ΔS and ΔV together with the ordering coefficient β . δC_p , $\delta\alpha$, and $\delta\kappa$ are not independent but from equation (8) we find the identity

$$\delta\kappa \cdot \delta C_p = TV(\delta\alpha)^2 \quad . \quad . \quad . \quad . \quad (9)$$

This can be used to reduce any thermodynamic expression involving the "excess" properties to one involving only two of them. We shall find it convenient to take $\delta\alpha$ and δC_p as the independent excess variables. Then from the elementary expression for the adiabatic compressibility

$$\kappa_s = \kappa - TV\alpha^2/C_p$$

we have

$$\delta\kappa_s = \delta\kappa - TV\delta(\alpha^2/C_p)$$

By use of eqn. (9) this can be thrown into the form

$$\delta\kappa_s/\bar{\kappa}_s = (\bar{\gamma} - 1)(\delta\alpha/\bar{\alpha} - \delta C_p/\bar{C}_p)^2 / [(\delta C_p/\bar{C}_p)(1 - \delta C_p/\bar{C}_p)] \quad . \quad (10)$$

where $\bar{\gamma} \equiv \bar{C}_p/\bar{C}_v$ is the ratio of the principal specific heats. The relation (10) will be used later.

The arguments just outlined could, of course, be carried through in terms of independent thermodynamic variables other than p and T . Indeed, it is an economy of expression (which will be found valuable later) not to be tied down to any special choice of variables. Let the independent thermodynamic variables (like p and T) be denoted by x and their conjugate dependent variables by X (note that x , for example, is a contracted way of referring to more than one quantity); we then have a free energy F such that

$$-dF = Xdx + Adz \quad . \quad . \quad . \quad . \quad (11)$$

$$\left. \begin{aligned} dX &= cdx + \lambda dz \\ dA &= \lambda' dx + \beta dz \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (12)$$

where c stands for the thermodynamic coefficients $(\partial X/\partial x)_z$, $\lambda (= \lambda')$ for the reaction coefficients $(\partial X/\partial z)_x$ and β for the ordering coefficient $(\partial A/\partial z)_x$. Eliminating dz from the two members of (12) we have

$$dX = (c - \lambda\beta^{-1}\lambda')dx + \lambda\beta^{-1}dA \quad . \quad . \quad . \quad (13)$$

The equilibrium coefficients $\bar{c} \equiv (\partial X/\partial x)_A$ appear as the coefficient of dx in eqn. (13) so that

$$\delta c = \bar{c} - c = -\lambda\beta^{-1}\lambda' \quad . \quad . \quad . \quad . \quad (14)$$

Equations (11)—(14) summarise the static thermodynamics of a relaxing or reacting system.

Rate Equations.—It is now necessary to consider the time-dependent behaviour of a relaxing system. We know that in equilibrium $A = 0$. It therefore seems reasonable to regard A as a kind of internal driving force acting on the system and, whenever A is non-zero, trying to change z so as to bring it back to equilibrium. The simplest rate assumption consistent with this idea is that the system satisfies the linear relation

$$dz/dt = LA \quad . \quad . \quad . \quad . \quad . \quad (15)$$

with L a constant. It may be helpful to note that this is precisely the assumption required by the Prigogine-de Groot theory of irreversible thermodynamics,⁸ since the rate of entropy production in the system can easily be shown to be $(dz/dt)(A/T)$. Moreover in the case of chemical reactions equation (15), although formally very different from the usual assumptions about forward and backward reaction rates, can in fact be shown to have equivalent macroscopic consequences.⁹ Instead of using L it is convenient to introduce a new rate parameter τ having the dimensions of time and defined by $\tau = -\beta^{-1}L^{-1}$. Then eqn. (15) can be written as

$$-\beta\tau dz/dt = A \quad . \quad . \quad . \quad . \quad . \quad (16)$$

To obtain the "thermodynamic equations of motion" which give the time-dependent law connecting x and X we must eliminate A and z from equations (12) and (16). This yields the form

$$dX = [c - \lambda(1 + \tau d/dt)^{-1}\beta^{-1}\lambda']dx \quad . \quad . \quad . \quad (17)$$

which, with eqn. (14), becomes

$$dX = \left(c + \frac{\delta c}{1 + \tau(d/dt)} \right) dx \quad . \quad . \quad . \quad (18)$$

or

$$dX = \left(\bar{c} - \frac{\delta c(d/dt)}{1 + \tau(d/dt)} \right) dx$$

These important relations give the dynamical behaviour of a relaxing system in a form convenient to use and remember. In order to see their significance let X and x be referred to equilibrium values of zero. Then we can write eqn. (18) in the form

$$X + \tau(dX/dt) = \bar{c}x + \tau c(dx/dt) \quad . \quad . \quad . \quad (19)$$

This shows that if a fixed "force" of x_0 be applied to the system (initially in equilibrium), the "response" $X(t)$ is an instantaneous jump of cx_0 followed by an exponential relaxation to the final response $\bar{c}x_0$ with a time-constant of τ . This is illustrated in Fig. 1.

Having obtained the general formula (18) in a somewhat contracted

⁸ Prigogine and Defay, "Thermodynamique Chimique", Desoer, Liège, 1950; de Groot, "Thermodynamics of Irreversible Processes", North Publ. Co., Amsterdam, 1951.

⁹ Davies and Lamb, *Proc. Phys. Soc.*, 1956, **69**, B, 293.

notation we may recover the appropriate dynamical equations with, say, p and T as independent variables. In the neighbourhood of an equilibrium

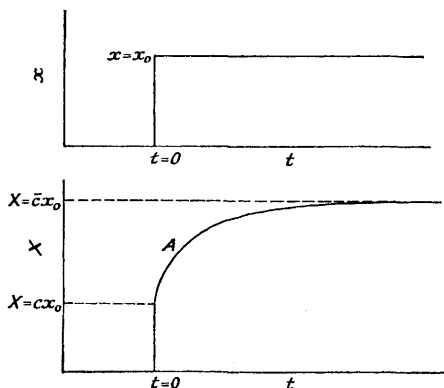


FIG. 1

Response of a relaxing system to a "step".

A, curve of $X/x_0 = c + (\bar{c} - c)[1 - \exp(-t/\tau)]$

state with co-ordinates V_0 , T_0 , etc., they may be written as

$$\left. \begin{aligned} S - S_0 &= \left\{ \left(C_p + \frac{\delta C_p}{1 + \tau(d/dt)} \right) / T_0 \right\} (T - T_0) \\ &\quad - \left\{ V_0 \left(\alpha + \frac{\delta \alpha}{1 + \tau(d/dt)} \right) \right\} (p - p_0) \\ V - V_0 &= \left\{ V_0 \left(\alpha + \frac{\delta \alpha}{1 + \tau(d/dt)} \right) \right\} (T - T_0) \\ &\quad - \left\{ V_0 \left(\kappa + \frac{\delta \kappa}{1 + \tau(d/dt)} \right) \right\} (p - p_0) \end{aligned} \right\} \quad (20)$$

Before using equations such as these to describe the behaviour of an actual system they must be supplemented by information giving the mechanical and thermal exchanges between the system and its environment. (For example, we might be required to describe the adiabatic approach to equilibrium in a constant-volume container. The left-hand sides of equations (20) then vanish and we are left with the integrable system of two equations for the two unknowns p and T .)

The derivation of eqn. (18) shows that we are not tied to any special independent variables. However it is important to notice that although the "dynamic" coefficients

$$c^* \equiv c + \delta c / [1 + \tau(d/dt)] \quad . \quad . \quad . \quad (21)$$

have always the same form, the value of τ depends on the choice of independent variables.⁹ Formally, this arises because $\beta = (\partial A / \partial z)_{p,T}$ is involved in the definition of τ so that a change in the choice of x generally implies a change in the value of τ . Thus, if we write $\tau_{p,T}$ for the value of τ appro-

appropriate when p and T are independent variables, etc., we have the dynamic expressions

$$\left. \begin{aligned} \kappa^* &= \kappa + \delta\kappa/[1 + \tau_{p,T}(d/dt)] \\ \kappa_S^* &= \kappa_S + \delta\kappa_S/[1 + \tau_{p,S}(d/dt)] \end{aligned} \right\} \dots \dots \dots (22)$$

The relations between various possible τ 's have been worked out. It can be shown for example that $\tau_{p,S} = (C_p/\bar{C}_p)\tau_{p,T}$.

Sound Propagation in a Relaxing Fluid.—Now that the dynamical relaxation behaviour of a simple "reacting" system has been established we can use the result to find the effect of the relaxation on the propagation of a sound wave.

Consider the propagation of a plane sound wave in the x -direction. Let u be the instantaneous velocity of a particle of the fluid. The net force per unit area acting on an element of the fluid of thickness δx is $-(\partial p/\partial x)\delta x$; the (mass \times acceleration) of the element is $\rho_0(\partial u/\partial t)\delta x$ where ρ_0 is the density. Hence by Newton's law of motion

$$\rho_0 \partial u/\partial t = - \partial p/\partial x \dots \dots \dots (23)$$

Let d be the dilatation of the fluid so that the mass included in unit area of thickness δx is $\rho_0(1 - d)\delta x$. This changes at a rate $-\rho_0\delta x \cdot \partial d/\partial t$ which must be equal to the net rate of flow of mass into the element, viz., $-\rho_0(\partial u/\partial x)\delta x$. Equating these two quantities we have the continuity equation

$$\partial u/\partial x = \partial d/\partial t \dots \dots \dots (24)$$

From equations (23) and (24) we find that

$$\partial^2 p/\partial x^2 = - \rho_0 \partial^2 d/\partial t^2 \dots \dots \dots (25)$$

and it remains to consider the equation of state of the fluid: it is at this point that the work of the previous sections is relevant. It can be shown that, except at frequencies so high as to be out of range of present experiment, the transmission of sound through a fluid is "adiabatic". This means that virtually no heat is transmitted down the temperature gradients which exist at any instant in the direction of the sound wave. Hence the relation between the pressure and the dilatation is the time-dependent adiabatic relationship implied by the second member of eqn. (22). It can be written in a form similar to that of eqn. (19):

$$d + \tau \frac{d}{dt} d + \bar{\kappa}_S p + \tau \kappa_S \frac{d}{dt} p = 0 \dots \dots \dots (26)$$

Here the " τ " is actually $\tau_{p,S}$ of eqn. (22). Eliminating d between equations (25) and (26) we have the wave equation in the form

$$\left(1 + \tau \frac{\partial}{\partial t}\right) \frac{\partial^2 p}{\partial x^2} = \rho_0 \left(\bar{\kappa}_S + \tau \kappa_S \frac{\partial}{\partial t}\right) \frac{\partial^2 p}{\partial t^2} \dots \dots \dots (27)$$

As usual we seek solutions of eqn. (27) having sinusoidal time variation of frequency $\omega/2\pi$ by substituting in it a solution proportional to $\Re \exp$

$[i(\omega\tau - kx)]$ and then solving the resultant equation for k . It is found that k must satisfy the characteristic equation

$$k^2/\omega^2 = \rho\bar{\kappa}_S(1 + i\omega\tau\kappa_S/\bar{\kappa}_S)/(1 + i\omega\tau)$$

$$= \frac{|k^2|}{\omega^2} \exp(-i\theta), \text{ say} \quad . \quad . \quad . \quad . \quad (28)$$

Thus the propagation number k is complex and the solution sought is proportional to $\mathcal{R}e \exp \{i[\omega t - |k| (\cos \theta/2)x] - |k| (\sin \theta/2)x\}$.

Consideration of the form of the solution shows that the phase velocity (c) or wavelength (λ) and the amplitude absorption coefficient per unit length (α) are given by

$$\left. \begin{aligned} c &= \omega/(|k| \cos \theta/2) \\ \lambda &= 2\pi/(|k| \cos \theta/2) \\ \text{or} \quad \alpha &= |k| \sin \theta/2 \end{aligned} \right\} . \quad . \quad (29)$$

The most convenient theoretical measure of the absorption is not α but the dimensionless absorption coefficient per wavelength (μ) which is given from eqn. (29) as

$$\mu \equiv \alpha\lambda = 2\pi \tan \theta/2 \quad . \quad . \quad . \quad . \quad (30)$$

Finally, $\tan \theta/2$ can be found from eqn. (28) so that

$$\mu = (2\pi/xr) \{ [1 + x^4(1-r)^2 + 2x^2(1-r) + x^2r^2]^{\frac{1}{2}} - 1 - x^2(1-r) \} \quad (31)$$

where $x = \omega\tau \equiv \omega\tau_{p,S}$ and $r = \delta\kappa_S/\bar{\kappa}_S$ —sometimes called the “relaxation strength”. The dependence of μ and of c on $\omega\tau$ is shown in Fig. 2 on a

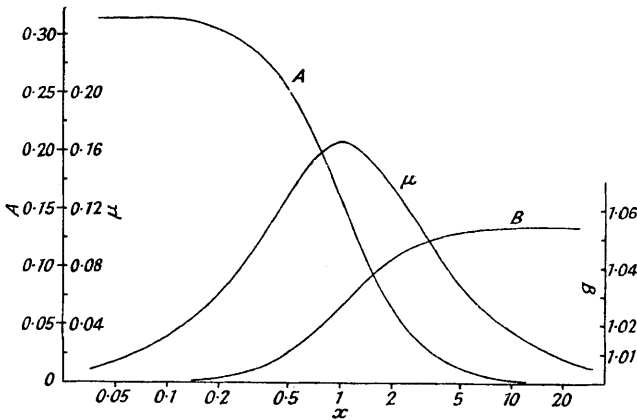


FIG. 2

Absorption and velocity associated with a single relaxation ($r = \delta K_S/K_S = 0.1$).

Curves of A, $(\alpha/f^2)[c_0 f_0 \sqrt{(1-r)}]$; B, c/c_0 and μ as functions of $x = \omega\tau$.

logarithmic scale for a moderate value of $\delta\kappa_S/\bar{\kappa}_S$ ($= 0.1$). The most conspicuous and important feature is the hump on the curve of μ . The maximum occurs at a frequency ω_{\max} given by

$$\omega_{\max}\tau_{p,S} = (1 - \delta\kappa_S/\bar{\kappa}_S)^{-\frac{1}{2}} . \quad . \quad . \quad . \quad (32)$$

and the value of the maximum is

$$\mu_{\max} = 4\pi \left\{ \left[1 + \frac{1}{4} \frac{(\delta\kappa_S/\bar{\kappa}_S)^2}{1 - \delta\kappa_S/\bar{\kappa}_S} \right]^{\frac{1}{2}} - 1 \right\} / \left\{ \frac{\delta\kappa_S/\bar{\kappa}_S}{(1 - \delta\kappa_S/\bar{\kappa}_S)^{\frac{1}{2}}} \right\} \quad (33)$$

The expression for μ_{\max} in eqn. (33) can be expanded in powers of

$$[(\delta\kappa_S/\bar{\kappa}_S)^2/(1 - \delta\kappa_S/\bar{\kappa}_S)].$$

In practice it generally happens that $\delta\kappa_S/\bar{\kappa}_S < 0.4$; then with an accuracy better than 1% we have

$$\mu_{\max} \approx \frac{\pi}{2} \frac{\delta\kappa_S/\bar{\kappa}_S}{(1 - \delta\kappa_S/\bar{\kappa}_S)^{\frac{1}{2}}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (34)$$

It is clear that equations (32) and (33) can be used to find the thermodynamic parameter $\delta\kappa_S/\bar{\kappa}_S$ and the rate parameter $\tau_{p,S}$ from reasonably accurate measurements of sound absorption as a function of frequency.

The Introduction of Chemical Reaction Parameters: Formulæ for Reactions in Ideal Solution.—The main interest in obtaining the parameter $\delta\kappa_S/\bar{\kappa}_S$ is that the work of p. 136 shows that it can be related to the reaction coefficients of chemical interest, ΔV and ΔS . Indeed, by eqn. (10) it may be expressed in terms of $\delta\alpha$ and δC_p together with certain measurable equilibrium properties of the fluid; $\delta\alpha$ and δC_p are in turn related to ΔV and ΔS by the formulæ of eqn. (8). The only other unknown quantity appearing in this chain is the ordering coefficient β . It is the object of this section to show how β can be found for the special case of reactions in ideal solution.

The definition of β and its expression in eqn. (3) show that β is a solution property of the system the evaluation of which depends on knowing the variations in chemical potential with composition. The simplest and most useful case to consider is that of the ideal solution specified by

$$\mu_i = \mu_i^\circ + RT \ln x_i$$

where x_i is the mole fraction of the i -th constituent. Equation (3) then becomes

$$\beta = -RT \{ \sum_i v_i^2/N_i - \nu^2/N \} \quad \cdot \quad \cdot \quad \cdot \quad (35)$$

where $\nu \equiv \sum_i v_i$ and $N \equiv \sum_i N_i$. The mole numbers N_i will be determined by the initial number of moles and the degree z to which the reaction has proceeded in equilibrium:

$$N_i = N_i^\circ + v_i z \quad \cdot \quad \cdot \quad \cdot \quad (36)$$

Finally z will be fixed by the equilibrium condition $\sum_i v_i \mu_i = 0$ which can be written as

$$\prod_i (N_i^\circ + v_i z)^{v_i} = (N^\circ + \nu z)^\nu \exp(-\Delta\mu^\circ/RT) \quad \cdot \quad \cdot \quad (37)$$

($\Delta\mu^\circ$ is often called $\Delta G^\circ = -RT \ln K$, the Gibbs free-energy change of the pure constituents at the same pressure and temperature.)

The expression for β comes from eliminating N_i , N , and z from equations (35), (36), and (37). Each case must be dealt with on its merits. The two most important ones are:

(i) The unimolecular reaction, $-M_1 + M_2 = 0$ with $\nu_1 = -1$, $\nu_2 = 1$.

Here we find that

$$-\beta = \frac{RT}{(N_1^\circ + N_2^\circ)} \cdot \frac{[1 + \exp(\Delta G^\circ/RT)]^2}{\exp(\Delta G^\circ/RT)} \quad . \quad . \quad (38)$$

(ii) The dimerisation reaction, $-M_1 + 2M_2 = 0$ with $\nu_1 = -1$, $\nu_2 = 2$. In this case*

$$-\beta = \frac{RT}{(2N_1^\circ + N_2^\circ)} \cdot \frac{[1 + 4 \exp(\Delta G^\circ/RT)]^{3/2}}{\exp(\Delta G^\circ/RT)} \quad . \quad . \quad (39)$$

Application and Summary of the Theory.—In order to make clear the practical use of the material of the last three sections we shall now consider how one could start from absorption data taken over reasonably wide bands of frequency and temperature and make inferences concerning the reaction mechanism responsible for the absorption. We shall assume that appropriate corrections have already been made for the “classical” absorption due to viscosity and thermal conductivity and that we are left with experimental values for $\mu(\omega, T)$ due to relaxation only.

We must first check that the frequency dependence has the correct form [eqn. (31)] for a single relaxation mechanism. If so, we may consistently make

ASSUMPTION 1: The relaxation is due to a single mechanism.

Without any further assumption we then obtain the two macroscopic parameters associated with the mechanism, ΔV and ΔS . Take the maximum value of μ at a given temperature [$\mu_{\max}(T)$] and the corresponding frequency [$\omega_{\max}(T)$].

(i) Let us write $m \equiv 2\mu_{\max}/\pi$. Then from eqn. (33) the thermostatic parameter $r(T) \equiv \delta\kappa_S/\bar{\kappa}_S$ is given by

$$r(T) \equiv \delta\kappa_S/\bar{\kappa}_S = m \left\{ (1 + \frac{1}{4}m^2)^{\frac{1}{2}} - \frac{1}{2}m \right\} \quad . \quad . \quad (40)$$

This is the only piece of thermostatic (as opposed to kinetic) information obtainable directly from experiment.

(ii) A kinetic parameter $\tau(T)$ —the adiabatic-isobaric relaxation time—characteristic of the mechanism is obtained from eqn. (32) which with the help of (40) can be written as

$$1/\tau^2 = \omega_{\max}^2 \left\{ 1 - m(1 + \frac{1}{4}m^2)^{\frac{1}{2}} + \frac{1}{2}m^2 \right\} \quad . \quad . \quad (41)$$

Later we shall mention the Eyring-like discussions which are usually given in connection with observed values of $\tau(T)$. Here we wish to consider how $\delta\kappa_S/\bar{\kappa}_S$ (a function of T) can be used to obtain some thermostatic information. To do this we must first introduce a definite assumption about the stoichiometric nature of the mechanism. Let us take the simplest and most important case.

* In the case of dimerisation in solution with N_s° moles of solvent it follows from (35) and (37) that $Y = -(2N_1^\circ + N_2^\circ + N_s^\circ)\beta$ is the positive root of the quadratic equation:

$$Y^2\xi^2(1 - \frac{1}{2}\xi)^2/(K + 8\xi - 4\xi^2) = Y(1 - \xi) + (K + 4)^2/4K$$

where $\xi = (2N_1^\circ + N_2^\circ)/(2N_1^\circ + N_2^\circ + N_s^\circ)$, and $K = \exp(-\Delta G^\circ/RT)$. This equation gives the dependence of β on the strength of solution (ξ) and the equilibrium constant K .

ASSUMPTION 2: The reaction involved is the unimolecular reaction $-M_1 + M_2 = 0$ and it takes place in ideal solution.

This means that we may take over formula (38) for β which involves the unknown Gibbs energy change for the "pure constituents", ΔG° , depending in general on T . If this expression for β is substituted in eqn. (8) (remembering that $\Delta S = \Delta H^\circ/T$) we obtain δC_p , $\delta\alpha$, and $\delta\kappa$ in terms of the *three* reaction parameters ΔV° , ΔH° , and ΔG° . Thus eqn. (10) eventually expresses the measurable quantity $\delta\kappa_S/\bar{\kappa}_S$ from (40) in terms of these three unknown, temperature-dependent reaction parameters. The only relevant relation between them* is the Gibbs-Helmholz equation

$$\partial(\Delta G^\circ/T)/\partial T = -\Delta H^\circ/T^2 \quad . \quad . \quad . \quad (42)$$

It is clear that further assumptions must be made before information can be obtained about the reaction coefficients.

The simplest and commonest assumption is

ASSUMPTION 3: The volume change of the reaction (ΔV°) is zero.

For isomeric reactions this is often a very reasonable assumption because the kinds of molecular mechanism which have been studied do not usually involve large changes of size. It has immediate implication that $\delta\alpha = \delta\kappa = 0$. Hence $\delta\kappa_S$ can be expressed entirely in terms of δC_p and we find in fact from equations (40) and (10) that

$$\frac{\delta C_p}{\bar{C}_p} = \left\{ \frac{m}{(\bar{\gamma} - 1)(1 + m/4)^2 + m} \right\} \quad . \quad . \quad . \quad (43)$$

The right-hand side of eqn. (43) is an experimentally accessible function of temperature only. Returning now to equations (38) and (8) we have the final formula

$$\frac{\delta C_p}{R} = \Phi(T) = \frac{\bar{C}_p}{R} \left[\frac{m}{(\bar{\gamma} - 1)(1 + m/4)^2 + m} \right] = \left(\frac{\Delta H^\circ}{RT} \right)^2 \frac{\exp(\Delta G^\circ/RT)}{[1 + \exp(\Delta G^\circ/RT)]^2} \quad (44)$$

where $\Phi(T)$ is an experimentally accessible function of T and the right-hand side contains the unknown functions ΔG° and ΔH° , connected by eqn. (42). The system (42) and (44) can be integrated to give

$$\left. \begin{aligned} \Delta G^\circ(T) &= 4RT \tanh^{-1} \tan \frac{1}{2} \left\{ C + \int_{T_0}^T \sqrt{[\Phi(T)]} dT/T \right\} \\ \Delta H^\circ(T) &= 2RT \sqrt{[\Phi(T)]} \sec \left\{ C + \int_{T_0}^T \sqrt{[\Phi(T)]} dT/T \right\} \end{aligned} \right\} \quad (45)$$

where C is an arbitrary constant of integration. The ultrasonic data alone are therefore not sufficient to fix the reaction coefficients. It is nevertheless used to estimate them by making a further assumption.

ASSUMPTION 4: The entropy change of the reaction (ΔS°) (and *therefore* ΔH°) is independent of temperature.

The Gibbs energy change of the reaction is thus taken to be a linear

* If data at various pressures were available the relation $\partial \Delta G^\circ/p \partial = \Delta V^\circ$ would become relevant. We do not consider this case any further.

function of T , $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, and it becomes a question of fitting formula (44), which now involves two *constants* ΔH° and ΔS° , to the experimental results. It should be emphasized that even if the experimental data fit eqn. (44) exactly for an appropriate choice of ΔH° and ΔS° this does not *prove* the constancy of ΔH° and ΔS° but merely shows the consistency of assuming that they are constant: the integration constant of eqn. (45) cannot be removed by taking thought.

The simplest version of eqn. (44) occurs under the further specialisation of
ASSUMPTION 5: The entropy change of the reaction (ΔS°) is zero.

This is often quite a reasonable assumption. In any case the resulting form of eqn. (44)

$$\Phi(T) = \left[\frac{\Delta H^\circ}{RT} \right]^2 \frac{\exp(\Delta H^\circ/RT)}{(1 + \exp \Delta H^\circ/RT)^2} \quad (46)$$

usually gives a good qualitative picture of the variation of Φ (which is nearly proportional to μ_{\max}) with temperature. The form of eqn. (46) is shown in Fig. 3, where δC is the product of R and the right-hand side of eqn. (46). It is sometimes known as Schottky's function because it was

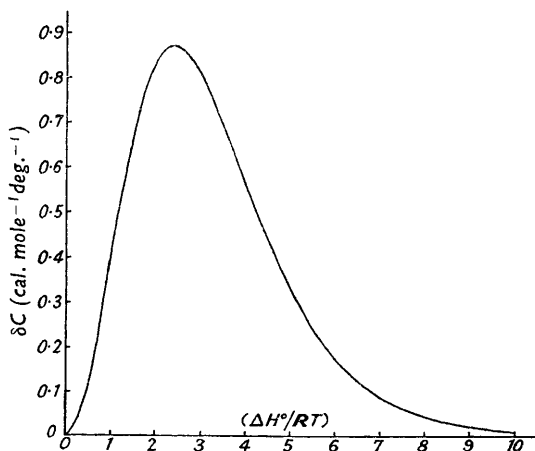


FIG. 3

The relaxing specific heat for a two-state equilibrium with $\Delta S^\circ = 0$.

introduced by him as the contribution to the specific heat due to a single excited energy state above a non-degenerate ground state. If the variation of μ_{\max} with temperature is known one can tell immediately whether ΔH° is larger or smaller than about $2.5RT$ (*i.e.*, 1.5 kcal./mole at 300°K).

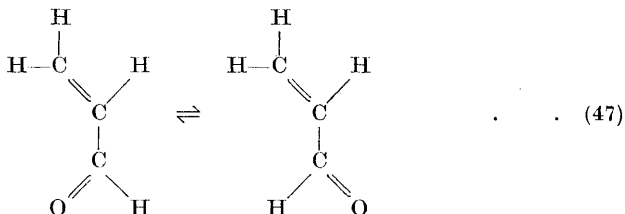
To sum up: under conditions and assumptions which we have attempted to display exactly, it is possible to use ultrasonic absorption measurements in order to obtain (i) an exact measurement of a relaxation time (τ) associated with simple molecular mechanisms, and (ii) reasonable estimates of the thermodynamic reaction coefficients (ΔH° and ΔS°) of these mechanisms.

Experimental investigations on ultrasonic absorption in liquids

Relaxation Due to Rotational Isomerism.—Whenever the molecules of a liquid can exist in two or more isomeric forms which differ in energy, then it is possible for the equilibrium to be perturbed by a sound wave in a manner discussed in the last section. Thus in the neighbourhood of the characteristic frequency f_c the absorption per unit wavelength (μ) passes through a maximum value which, for the two-state process with $\Delta V = 0$, is related to the energy difference between the two forms by eqn. (44). This equation shows that an essential requirement for the existence of an ultrasonic absorption due to the isomerism is that the different configurational forms of the molecule shall *differ in energy*. Although evidence for the existence of rotational isomers can be found from other measurements, for example from infrared studies, it appears that the strength of the ultrasonic relaxation is particularly sensitive to the number of molecules in the state of higher energy (N_2). Prominent relaxations have been observed in cases where less than 1% of the molecules reside in the upper state corresponding to ΔH° values of 3 kcal./mole or more. Further, as we have shown, it is possible to make reasonable estimates of ΔH° and ΔS° from experimental measurements of absorption over a range of temperature. This is not always possible by other methods.

The connection between observed ultrasonic absorption and the existence of different energy states due to rotation isomers has been established only recently so that many of the results available at present are of a preliminary nature. In many cases work has not been carried out over a sufficiently wide range of temperature to permit estimates of ΔH° and ΔS° , although the mechanisms responsible for the observed absorption can be described with reasonable certainty. However, the following cases will serve to illustrate the value of the ultrasonic method of investigating rotational isomerism. Once the mechanism responsible for the absorption has been established it is merely a question of extending the measurements over a sufficient range of temperature and frequency in order to obtain the reaction coefficients (p. 144).

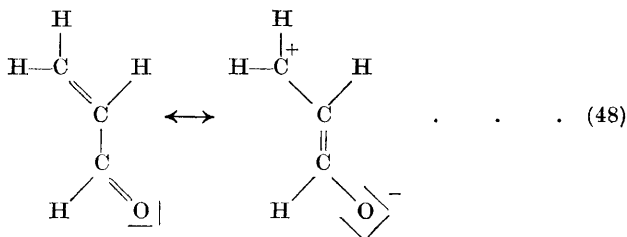
Unsaturated aldehydes and ketones. Acraldehyde ($\text{CH}_2\text{:CH-CHO}$) is a typical example of an unsaturated aldehyde in which a relaxation has been observed.¹⁰ This is attributed to a perturbation by the sound wave of the equilibrium (47):



These planar configurations of the molecule are stabilised by conjugation

¹⁰ de Groot and Lamb, *Trans. Faraday Soc.*, 1955, **51**, 1676; *Nature*, 1956, **177**, 1231.

of the bond between the central carbon atoms which can be regarded in terms of the resonating structures :



In this case the characteristic frequency of the relaxation at 25° is in the region of 250 Mc./sec. as is evident from Fig. 4, which includes details of other similar liquids. It has been suggested¹⁰ that the smaller the resonance

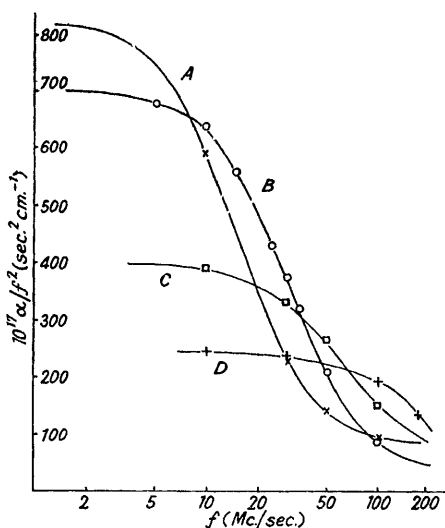


FIG. 4

Relaxation in unsaturated aldehydes.

A, Cinnamaldehyde (25°); B, crotonaldehyde (25°); C, crotonaldehyde (50°); acraldehyde (25° c).

[By courtesy of de Groot and Lamb, *Nature*, 1956, **177**, 1231.]

energy (*i.e.*, the weaker the conjugation) the smaller is the energy barrier which has to be overcome in bringing a molecule from a favourable position through a non-stabilised intermediate form to a second favourable position, and hence the higher is the characteristic frequency. The replacement of the hydrogen in the *trans*-position on the top carbon atom by a methyl group to form crotonaldehyde ($\text{CH}_3\text{:CH:CH:CHO}$) strengthens the conjugation and lowers the characteristic frequency from somewhat above 200 Mc./sec. for acraldehyde to 30 Mc./sec. for crotonaldehyde at the same

temperature. This effect of stronger conjugation can be offset by an increase in steric hindrance if, for example, the hydrogen of the aldehyde group is itself replaced by a methyl group to form a ketone. An interesting case arises in mesityl oxide $[(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3]$ where no relaxation is observed over the entire frequency range 250 kc./sec. to 200 Mc./sec., the corresponding value of (α/f^2) being constant at $34 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$ for a temperature of 25° C . However, construction of a scaled molecular model for mesityl oxide shows that the higher-energy state to the right of the corresponding equilibrium (47) is untenable owing to the physical size of the interacting methyl groups. The absence of any relaxation in this case substantiates the molecular interpretation described above. A comprehensive study has been made of the ultrasonic absorption in these and other related liquids and will shortly be published. A summary of the results at present available is given in Table 1.

TABLE 1. *Sound absorption parameters for certain aldehydes*

	Temp.	$10^{17} A$ (sec. ² cm. ⁻¹)	$10^{17} B$ (sec. ² cm. ⁻¹)	f_c (Mc./sec.)	$10^{-6} C$ (cm. sec. ⁻¹)	$10^2 \mu_{\text{max}}$
Croton- aldehyde	25°	674	29	30.3	1.268	1.29
	50	355	34	70.0	1.165	1.45
Cinnam- aldehyde	25	722	78	15.7	1.561	0.885
Mesityl oxide	25	No relaxation ; $\alpha/f^2 = 34 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$				

Esters. Ultrasonic relaxation has been observed in a number of esters,^{11, 12} a summary of the relaxation parameters for four such liquids being given in Table 2.

TABLE 2. *Relaxation parameters for four esters*

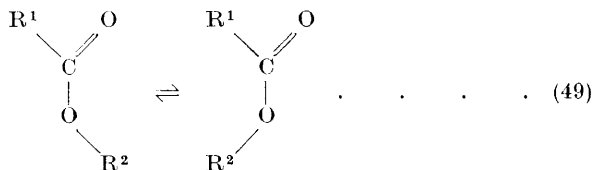
Liquid	Temp.	f_c (Mc./sec.)	$10^2 \mu_{\text{max}}$
Methyl formate	25°	0.35	3.1
Ethyl formate	25	0.40	4.8
Methyl acetate	20	6.8	0.072
Ethyl acetate	20	11.8	0.020

The explanation of these relaxations is that the sound wave perturbs an equilibrium of the form (49). These planar positions of the molecule

¹¹ Pinkerton, Ultrasonics Conference, Brussels, 1951, p. 117 (*Med. Vlaamsche Akad. k. Wet.*); Huddart, Thesis, London, 1950; Biquard, *Ann. Physique*, 1936, **6**, 195; Liebermann, *Phys. Rev.*, 1949, **75**, 1415; 1949, **76**, 440.

¹² Karpovich, *J. Chem. Phys.*, 1954, **23**, 1767.

are stabilised by conjugation of the carbon-oxygen bond which is possible owing to the lone-pair electrons of the oxygen atoms.



Measurements over an extended temperature range are available only for ethyl acetate for which $\Delta H^\circ \approx 3$ kcal./mole whilst the activation energy in the backward direction (see p. 158) is $\Delta H_2^\ddagger = 5.7$ kcal./mole. The value of ΔH° is consistent with the fact that μ_{\max} increases with increasing temperature and the value of δC_p is therefore on the right of the hump in the specific-heat curve for a 2-state equilibrium (Fig. 3). An increase in the size of the groups R^1 and R^2 diminishes μ_m and therefore increases ΔH° . A marked increase in characteristic frequency is found in passing from a formate ($\text{R}^1 = \text{H}$) to a corresponding acetate ($\text{R}^1 = \text{CH}_3$) owing, presumably, to increased steric interaction. On the other hand only a slight increase in f_c is found in passing from the methyl ester ($\text{R}^2 = \text{CH}_3$) to the corresponding ethyl ester ($\text{R}^2 = \text{C}_2\text{H}_5$): in this case increased conjugation of the C-O bond partially offsets the effect of increased steric interaction on the variation of f_c .

cycloHexane derivatives. Pronounced relaxation occurs in certain derivatives of *cyclohexane* with characteristic frequencies in the neighbourhood of 100 to 200 kc./sec.^{12, 13} Owing to the limited accuracy of the reverberation technique which is employed to measure the absorption in liquids at these relatively low frequencies it has not been thought worth while to make measurements at different temperatures. The molecular mechanism responsible for the observed relaxations at room temperatures is, however, clearly defined and it is to be hoped that further efforts to improve the experimental accuracy will be successful, thus permitting direct evaluation of the energy parameters.

Both "boat" and "chair" forms of *cyclohexane* are possible although the "boat" form does not appear to be present in appreciable proportions under ordinary conditions.^{14, 15} No relaxation has been observed in *cyclohexane* for frequencies up to 100 Mc./sec.¹⁶ from which it can be inferred that the population in the higher-energy "boat" form is very small indeed; the conversion from "boat" into "chair" form is extremely rapid. There is however a suggestion of incipient relaxation in the region of 200 Mc./sec.¹⁶

Directing attention to the chair form of the molecule, we must distinguish between one set of axial C-H bonds which are parallel to the

¹³ Lamb and Sherwood, *Trans. Faraday Soc.*, 1955, **51**, 1674.

¹⁴ Pitzer *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 977, 2488; Hassel, *Research*, 1950, **3**, 504.

¹⁵ McCoubrey and Ubbelohde, *Quart. Rev.*, 1951, **5**, 364.

¹⁶ Heasell and Lamb, *Proc. Phys. Soc.*, 1956, **69**, B, 869.

principal axis of the carbon ring and the other set of six C-H bonds which make an angle of $109^{\circ} 28'$ with this principal axis, the latter being termed equatorial bonds. If now a methyl group is substituted for a hydrogen atom then the two alternative "chair" forms, Fig. 5, are of different energy. The calculated energy difference for methylcyclohexane is 1.6 kcal./mole.

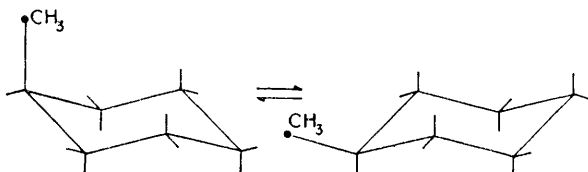


FIG. 5

Alternative "chair" forms for methylcyclohexane.

It is this equilibrium which is perturbed by the sound wave giving rise to the observed relaxations. Since in *cyclohexane* and 1:1-dimethylcyclohexane the alternative chair forms are of equal energy there is no observed relaxation. The corresponding absorption values at 25° are

$$(\alpha/f^2) = 192 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$$

for *cyclohexane* and $127 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$ for 1:1-dimethylcyclohexane. In the case of methylcyclohexane at 16° the (α/f^2) value falls from $200,000 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$ at very low frequencies (below 100 kc./sec.) to $118 \times 10^{-17} \text{ sec.}^2 \text{ cm.}^{-1}$ at 100 Mc./sec.

Measurements have been made on a complete series of dimethylcyclohexanes. An analysis of the results is given in Table 3. No relaxation was observed in *cis*-1:2-, *trans*-1:3-, and *cis*-1:4-dimethylcyclohexane since in each of these cases rotation of one methyl group from an axial to an equatorial position is accompanied by rotation of the second methyl group in the reverse direction (equatorial to axial). In the case of *cis*-1:3-dimethylcyclohexane the methyl groups in the higher energy (axial) positions encounter considerable steric interaction since both are on the same side of the plane of the carbon ring. An energy difference of order 5 kcal./mole has been assigned to the isomers of this molecule so that the expected relaxation is presumed to occur at very high frequencies, outside the present range (as for example with the "boat" and "chair" process for *cyclohexane*).

It is noteworthy that a relaxation has been observed in *cyclohexene*¹⁵ which has been attributed to perturbation of the equilibrium between the boat and *pseudo*-chair forms. The double carbon-carbon bond in *cyclohexene* causes the two hydrogen atoms pointing together from the "fore" and "aft" positions in the boat form to be further apart than in *cyclohexane*. The consequent reduction in steric interaction may explain why this type of relaxation is found in *cyclohexene* but not in *cyclohexane* where it presumably occurs at frequencies above 200 Mc./sec.

In connection with these relaxation processes mention should be made

of measurements recently reported for the shear viscosity of ethylcyclohexane as a function of frequency.¹⁷ The shear viscosity of the liquid has been found to decrease with increasing frequency over the same range in which the ultrasonic relaxation occurs. It is very likely that the change in shear viscosity arises from the same molecular mechanism as is responsible

TABLE 3. *Sound absorption in cyclohexane and its derivatives*

<i>cyclo</i> Hexane	Temp.	f_c (kc./sec.)	$10^{17} A$ (sec. ² cm. ⁻¹)	$10^{17} \alpha/f^2$ (sec. ² cm. ⁻¹) (150 to 40 kc./sec.)	$10^{17} \alpha/f^2$ (sec. ² cm. ⁻¹) 100 Mc./sec. and 25°)	μ_{\max}
Unsubstituted . . .	25°	No relaxation		197	192	—
Methyl-	16	140	200,000	—	118	0.017
Ethyl-	16	60	500,000	—	—	0.019
1 : 1 : 3-Trimethyl- . .	16	Relaxation above 1 Mc./sec.		2000	—	—
<i>cis</i> -1 : 2-Dimethyl- . .	16	No relaxation observed		<300	—	—
<i>trans</i> -1 : 2-Dimethyl- . .	16	120	55,000	—	78	0.004
<i>cis</i> -1 : 3-Dimethyl- . .	No relaxation observed				102	—
<i>trans</i> -1 : 3-Dimethyl-	No relaxation observed				84.6	—
<i>cis</i> -1 : 4-Dimethyl- . .	No relaxation observed				87.6	—
<i>trans</i> -1 : 4-Dimethyl-	16	150	26,000		112	0.0023

for the ultrasonic behaviour described above. Physically it is possible to visualise that in shearing motion preference would be given to that chair form in which the C-CH₃ bond is in the plane of the carbon ring. These preliminary results on the variation of shear viscosity with frequency are particularly interesting and it is hoped that this aspect will receive further attention in future work.

Triethylamine. Measurements of sound absorption in triethylamine over the frequency range 23 to 192 Mc./sec. and at temperatures from 25° c to 70° c have demonstrated the existence of a relaxation process which is attributed to the presence of rotational isomers.¹⁸ Curves of absorption at selected temperatures are shown in Fig. 6. Analysing the results in the

¹⁷ Clausnizer and Kneser, International Commission on Acoustics, 2nd Congress, 1956, Paper I.B.2.

¹⁸ Heasell and Lamb, *Proc. Roy. Soc.*, 1956, A, **237**, 233.

manner discussed earlier, we find that $\Delta H^\circ = 3.4$ kcal./mole and $\Delta S^\circ = 4.7$ cal./(mole deg.). Accordingly the experimental region is to the right of the hump in the specific-heat curve (Fig. 3) : μ_{\max} increases with increasing

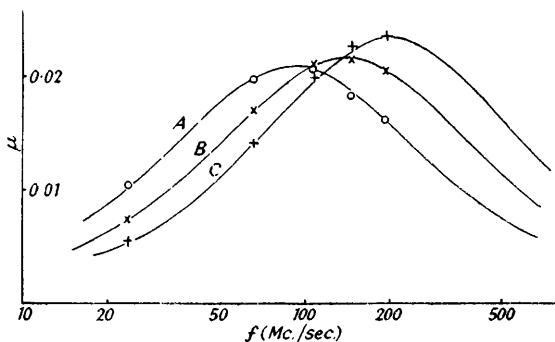


FIG. 6

Absorption in triethylamine.

The curves are theoretical and the points experimental. A 25°, B 35°, C 45° c.

[By courtesy of Heasell and Lamb, *Proc. Roy. Soc.*, 1956, A, 237, 233.]

temperature. The activation energy associated with the backward reaction is $\Delta H_2^\ddagger = 6.8$ kcal./mole (see p. 158). A study of the molecular model of triethylamine reveals the existence of three possible configurations shown in Fig. 7. It is considered that the equilibrium between two or possibly

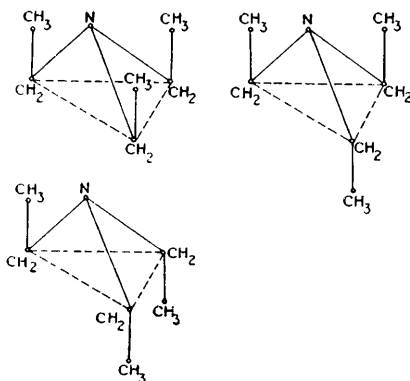


FIG. 7

Rotational isomers of triethylamine.

[By courtesy of Heasell and Lamb, *Proc. Roy. Soc.*, 1956, A, 237, 233.]

three of the configurational states is responsible for the relaxation. It is noteworthy that no evidence was found for relaxation in diethylamine where the two ethyl groups can be accommodated in the basal plane: this is not possible in triethylamine as can be readily verified from a molecular model. Additional support for this explanation is given in ref. 18.

Methylbutanes. The simplest type of rotational isomerism is due to alternative orientations of groups around the carbon-carbon bond in ethane and substituted ethanes and has been described in a previous Review.¹⁵ In these types of molecule there are, in general, three equilibrium positions which may or may not differ in energy depending upon the symmetry arrangements. Where energy differences exist between the alternative states it is to be expected that this will give rise to ultrasonic relaxation, as has been demonstrated.¹⁹ It appears that in order to observe the relaxation peak at convenient frequencies of the order of 10 Mc./sec. it is necessary to work at temperatures near 200° K. Relaxation was observed for 2-methylbutane, 2 : 3-dimethylbutane, and also for 2-methylpentane but was not found for 2 : 2-dimethylbutane where the three equilibrium states are of equal energy, nor for the straight-chain compound *n*-pentane. Typical results for 2-methylbutane are shown in Fig. 8, from which it is evident

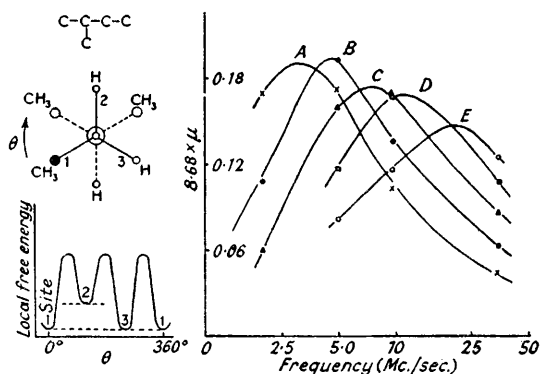


FIG. 8

Sound absorption in 2-methylbutane.

A 180°, B 190°, C 200°, D 210°, E 220° K. μ in this Fig. is in decibels per wavelength.

[By courtesy of Young and Petrauskas, *J. Chem. Phys.*, 1956, 25, 943.]

that as the temperature increases from 180° K the value of μ_{\max} increases initially and then falls with subsequent temperature increase above 190° K. This behaviour is characteristic of the specific-heat curve for a two-state process and indicates that the maximum in the specific heat (δC_p) occurs around 185° K. Since the maximum corresponds approximately to the condition $\Delta H^\circ/RT = 2.5$ it follows that ΔH° is approximately 0.9 kcal./mole. Activation energies for the relaxations in 2-methylbutane and 3-methylpentane were found to be about 4.7 kcal./mole: a value of 3.3 kcal./mole was found for 2 : 3-dimethylbutane. In a mixture of 3-methylbutane and *n*-pentane the curve of absorption against temperature exhibits a peak at the same temperature as that in pure 3-methylpentane but reduced in proportion to the reduction in the number of molecules of 3-methylpentane

¹⁹ Young and Petrauskas, *J. Chem. Phys.*, 1956, 25, 943; Chen and Petrauskas, *ibid.*, in the press.

which are present in the mixture. This simple behaviour in solution confirms that the reaction is unimolecular.

It is significant that in these liquids, as in the other cases of rotational isomers previously discussed, the observed relaxations can be described by a single relaxation time in each case. This fact alone could perhaps be used as evidence for an *intra*- as distinct from an *inter*-molecular equilibrium as the mechanism responsible for the relaxations.

Vibrational Relaxation.—The majority of ultrasonic investigations in gases have been concerned with relaxation due to the time-delay in establishing equilibrium of the internal vibratory motions of the molecules. In practically all cases it has been found that the observed relaxation involves the *whole* of the vibrational specific heat and is characterised by a single relaxation time. The explanation which is accepted at present is that the energy is coupled into the molecule *via* the mode of lowest vibrational frequency and then spreads rapidly to the other vibrational modes. Physically the time-delay in establishing equilibrium is due to the fact that many collisions are required for the molecule to lose one quantum of vibrational energy.

Effects of a similar nature are to be expected in liquids and the relatively high values of (α/f^2) for non-polar liquids are attributed to this mechanism. In liquids, however, the vibrational relaxation time is markedly affected by dipole interactions so that in general it is only possible to observe this type of relaxation in non-polar liquids; methylene chloride (results for which are discussed later) is an exception.

Carbon disulphide. A complete analysis is available for carbon disulphide which has a characteristic frequency of 78 Mc./sec. at 25° c.⁵ The relaxation at both 25° and -63° is characterised by a single relaxation time and involves the whole of the vibrational specific heat. The corresponding curves of absorption per unit wavelength are given in Fig. 9. There are

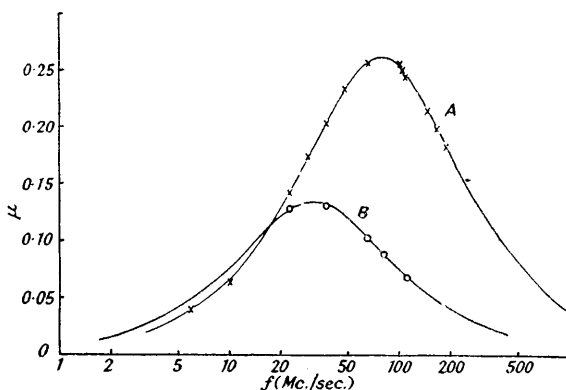


FIG. 9

Relaxation of the vibrational specific heat of carbon disulphide at (A) 25° and (B) 63° c.

The curves are theoretical and the points experimental.

[From results of Andreae, Heasell, and Lamb, *Proc. Phys. Soc.*, 1949, **60**, B, 625.]

three vibrational modes of this molecule and the total vibrational specific heat (δC) is obtained by summing the Einstein specific-heat contributions of each mode: $\delta C = \sum n R x^2 e^{-x} / (1 - e^{-x})^2$, where $x = h\nu/kT$ and the degeneracy factor, n , is unity for the two stretching vibrations and 2 for the bending vibration. Table 4 shows the excellent agreement found between the calculated values of μ_{\max} obtained on this basis and those derived from experiments by fitting the best single relaxation-time curve to the measured absorption values after allowing for the velocity dispersion.

TABLE 4. *Relaxation parameters for carbon disulphide*

Temp.	f_c (Mc./sec.)	μ_{\max} (expt.)*	μ_{\max} (calc.)*	δC [cal./ (mole deg.)]
25°	78	0.262	0.260	3.933
- 63	31	0.134	0.133	2.683

* This is the contribution of the relaxing process; it forms the major part of the total absorption per unit wavelength. The "classical" absorption due to shear viscosity has been subtracted from the measured absorption before making the above comparison with theory.

Benzene. Incipient relaxation has been observed in benzene¹⁶ as shown in Fig. 10. The results at present available do not cover a sufficient portion

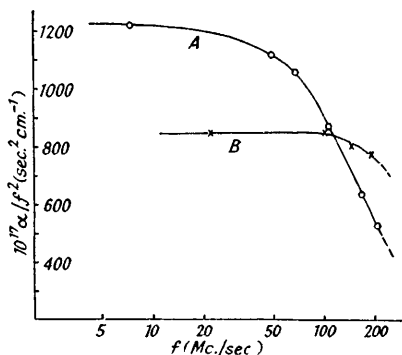


FIG. 10

Vibrational relaxation in (A) methylene dichloride and (B) benzene at 25° c.

[From results of Heasell and Lamb, *Proc. Phys. Soc.*, 1956, **69**, B, 869, and Andreae, *ibid.*, 1957, **70**, B, 71.]

of the relaxation region to permit an analysis to be made but it is presumed that the effect is due to relaxation of the vibrational specific heat. This question can be resolved only by measurements at higher frequencies.

Methylene dichloride. The relaxation observed in liquid methylene dichloride²⁰ is of interest since this is the only compound in which a multiple dispersion region has been established in the gas phase. In methylene dichloride vapour there are two dispersion regions²¹ and it is concluded that the lower-frequency relaxation involves all the vibrational modes

²⁰ Andreae, *Proc. Phys. Soc.*, 1957, **70**, B, 71.

²¹ Sette, Busala, and Hubbard, *J. Chem. Phys.*, 1955, **23**, 787.

except the mode of lowest infrared frequency which is itself responsible for the higher-frequency relaxation. It appears that a similar pattern of behaviour occurs in the liquid. The observed relaxation (Fig. 10) (of which only part has been covered experimentally) can be accounted for by all the vibrational modes except that of the lowest infrared frequency. Further experiments at different temperatures should help to clarify this point.

Carboxylic Acids.—Historically, acetic and propionic acids were the first liquids in which ultrasonic relaxation was observed and for which complete series of experimental results are available covering a substantial part of the relaxation (μ) curve at different temperatures.²² The values of f_c and μ_{\max} are given in Table 5 for an approximate temperature at 20° C. The Table also includes reaction parameters associated with the relaxation, assuming (see p. 144) that we have a unimolecular reaction in ideal solution with constant values of ΔH° and ΔS° .

TABLE 5. *Sound absorption in carboxylic acids near 20° C*

Liquid	f_c (Mc./sec.)	μ_{\max}	ΔH° (kcal./mole)	ΔS° [cal./(mole deg.)]	ΔH_2^\ddagger (kcal./mole)
Formic acid .	1.33	0.035	—	—	—
Acetic acid .	0.556	0.051	2.3	3.9	8.5
Propionic acid	2.02	0.013	3.9	4.4	7.5

It is known that acetic acid forms double molecules united by two hydrogen bonds in both the vapour and the liquid phase, although the heat of reaction is only known reliably for the vapour phase and for dilute solutions in non-polar solvents. It is natural therefore to consider the possibility that the relaxation is due to perturbation of the monomer-dimer reaction namely $A_1 + A_1 \rightleftharpoons (A_1)_2$; $2\text{CH}_3 \cdot \text{CO}_2\text{H} \rightleftharpoons (\text{CH}_3 \cdot \text{CO}_2\text{H})_2$. Using this equation, which is of the first order to the left and second order to the right, Freedman²³ has found approximate agreement between the ΔH° value which is obtained from analysis of the experimental results and that estimated for the pure acid using an extrapolation of the Moelwyn-Hughes formula $\Delta H^\circ_{\text{solution}} = \Delta H^\circ_{\text{vapour}} \times (\epsilon + 2)/3\epsilon$ where ϵ is the dielectric constant of the solvent. Freedman then uses the value $\epsilon = 7.1$ for acetic acid in this formula. Although the latter procedure is somewhat dubious, the agreement between the two values of ΔH° is good and until recently the conclusion was accepted that the relaxation in acetic acid, and possibly also in the other carboxylic acids, was due to perturbation of the monomer-dimer reaction. However, in order to clarify this issue measurements have recently been made of the absorption in solutions of acetic acid.²⁴ It was found that a second relaxation region occurs predominantly at low concentrations of acetic acid and with a characteristic frequency an order of

²² Lamb and Pinkerton, *Proc. Roy. Soc.*, 1949, A, **199**, 114; Lamb and Huddart, *Trans. Faraday Soc.*, 1950, **46**, 540.

²³ Freedman, *J. Chem. Phys.*, 1953, **21**, 1784.

²⁴ Piercy and Lamb, *Trans. Faraday Soc.*, 1956, **52**, 930.

magnitude higher than that for the pure acid. This second relaxation has been associated with the monomer-dimer reaction which leaves the explanation for the relaxation in pure acetic acid still open to question. One possibility is that in the pure acid the process responsible is the breaking of a single hydrogen bond which is supported by evidence that hydrogen links are formed in crystalline formic acid, as distinct from double molecules.²⁵

Rate parameters : frequency factor and activation energy

In cases where the relaxation strength is small, corresponding to a velocity dispersion of, say, less than 1%, it is unnecessary to distinguish between the various relaxation times $\tau_{p,S}$, $\tau_{p,T}$, etc., and for a unimolecular relaxation with $\Delta V = 0$ a single mean relaxation time $\tau = (k_{12} + k_{21})^{-1}$ can be used without further qualification. Then the characteristic frequency is $f_c = (k_{12} + k_{21})/2\pi$. Let the free energies of activation in the forward and reverse directions be, respectively

$$\Delta G_1^\ddagger = \Delta H_1^\ddagger - T\Delta S_1^\ddagger$$

$$\Delta G_2^\ddagger = \Delta H_2^\ddagger - T\Delta S_2^\ddagger$$

Then on a rate-theory basis the transition rates would be written

$$k_{12} = \left(\frac{kT}{h}\right) \exp(\Delta S_1^\ddagger/R - \Delta H_1^\ddagger/RT)$$

$$k_{21} = \left(\frac{kT}{h}\right) \exp(\Delta S_2^\ddagger/R - \Delta H_2^\ddagger/RT)$$

The equilibrium constant $K = k_{12}/k_{21} = \exp(-\Delta G^\circ/RT)$. Provided that $\Delta G^\circ/RT < 3$, say, k_{12} can be neglected in comparison with k_{21} to within 5% and then

$$f_c \approx k_{21}/2\pi = (1/2\pi)(kT/h) \exp(\Delta S_2^\ddagger/R - \Delta H_2^\ddagger/RT) \\ = (F_2/2\pi)(kT/h) \exp(\Delta H_2^\ddagger/RT)$$

where $F_2 = \exp(\Delta S_2^\ddagger/R)$.

The heat of activation ΔH_2^\ddagger in the reverse direction is thus given by

TABLE 6. *Activation energies, activation entropies, and frequency factors for various liquids near 20° C*

	ΔH_2^\ddagger (kcal./mole)	F_2	ΔS_2^\ddagger [cal./(mole deg.)]
Acetic acid	8.5	1.2	+ 0.37
Propionic acid	7.5	0.8	- 0.45
Crotonaldehyde*	5.5	0.3	- 2.1
Cinnamaldehyde*	5.6	0.2	- 3.0
Ethyl ac	5.7	0.2	- 3.2
Triethylamine	6.8	9.4	+ 4.5
Toluene†	8.5	0.31	- 2.3
2-Methylbutane	4.7	1.6	+ 0.9

* Calculations from recent results of Mr. M. S. de Groot.

† Beyer, *J. Acoust. Soc. Amer.*, 1955, **27**, 1.

²⁵ Holtzberg, Post, and Fankuchen, *Acta Cryst.*, 1953, **6**, 127.

the slope of the line representing a plot of $\log(f_c/T)$ against $1/T$. A summary of values is given in Table 6 from which it is evident that the factor F_2 is within an order of magnitude of unity in all these cases. Carbon disulphide cannot be considered in this light since the vibrational relaxation is not a 2-state process. Nevertheless, it is perhaps worth noting that if the experimental results are treated in this fashion one arrives at the values : $\Delta H_2^\ddagger = 1$ kcal./mole, $F_2 = 0.3 \times 10^{-3}$. The large discrepancy between this value for F_2 and those in Table 6 shows that if the cause of a relaxation is sought and the estimated F_2 is of the order of unity it is very unlikely that the relaxation is one of vibrational energy transfer. This fact seems to illustrate that the cause of the relaxation in toluene must be found in an explanation other than that of vibrational energy.

Experimental investigations on solutions

A significant feature of the sound absorption in binary mixtures of liquids is the shape of the curve of α/f^2 against concentration. If the experimental results refer to frequencies which are well removed from a relaxation region then at any particular concentration α/f^2 will be independent of frequency. In these circumstances four main patterns of behaviour can be distinguished.

Type A. Sagging curves of (α/f^2) versus concentration of the type shown in Fig. 11 are obtained for mixtures of liquids which are not associated

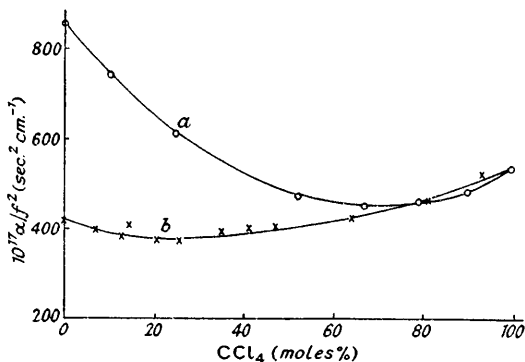


FIG. 11

Absorption in solutions of Type A; (a) benzene and (b) chloroform, in carbon tetrachloride at 25° C.

[By courtesy of Sette, *Nuovo cim. (Suppl.)*, 1950, 7, 318.]

either in the pure state or in the mixture, *e.g.*, for a mixture of two non-polar liquids.²⁶ If α/f^2 for liquid X is much greater than α/f^2 for liquid Y deeply sagging curves of type (a) are found whilst liquids of almost equal absorption generally exhibit rather flat curves of type (b). It is assumed that the major loss in each liquid is due to relaxation of the vibrational specific heat and the observed results are in reasonable agreement with theory.

²⁶ Sette, *Nuovo cim. (Suppl.)*, 1950, 7, 318.

Type B. If the mixture consists of molecules X and Y which associate with each other then the curve of (α/f^2) against concentration may exhibit a large hump at some intermediate concentration. It has been suggested that this effect is related to an interaction between the molecules of the

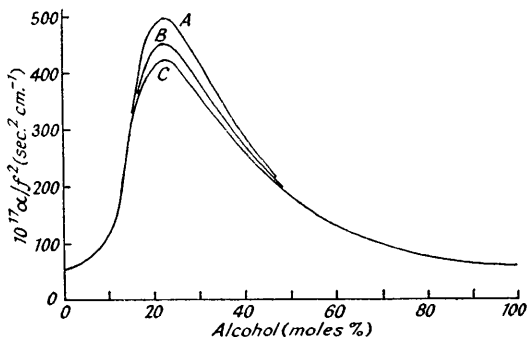


FIG. 12

Absorption in solutions of Type B; ethyl alcohol in water.

A 22.5, B 37.5, C 52.5 Mc./sec.

[By courtesy of Storey, *Proc. Phys. Soc.*, 1952, **65**, B, 943.]

two species as, for example, in the case of ethyl alcohol–water mixtures²⁷ (Fig. 12). On the other hand the view has also been put forward that this type of behaviour may be associated with the phenomenon of critical mixing²⁸ (see Type D).

Type C. Consider a mixture of two liquids X and Y with the following properties: the molecules of X do not associate either mutually or with molecules of type Y, whilst the molecules of Y associate with each other

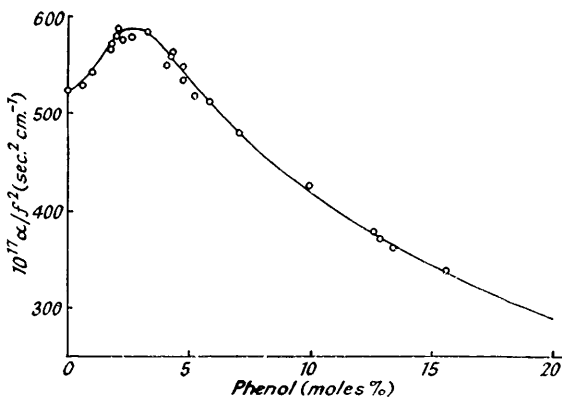


FIG. 13

Absorption in solutions of Type C; phenol in carbon tetrachloride.

[By courtesy of Maier and Mcz, *Z. Naturforsch.*, 1952, **7a**, 300.]

²⁷ Storey, *Proc. Phys. Soc.*, 1952, **65**, B, 943.

²⁸ Piercy, International Commission on Acoustics, 2nd Congress, 1956, paper I.B.8.

but not with those of type X. In such a mixture the (α/f^2) versus concentration curve may exhibit a small peak at low concentrations of Y as for example in a mixture of phenol and carbon tetrachloride²⁹ (Fig. 13). This effect is attributed to the association of molecules of type Y as for instance in a monomer-dimer equilibrium.

Type D. In a number of cases a critical mixing phenomenon occurs so that the liquids X and Y are only partially soluble in each other. For temperatures above the solubility curve the liquids are completely miscible whilst below this curve they separate into layers of each other. In these circumstances a pronounced maximum in the curve of (α/f^2) against concentration occurs at temperatures near the consolute temperature and this is attributed to the formation of molecular clusters. A typical example is shown in Fig. 14 for nitrobenzene in *n*-hexane.³⁰ A surprising feature

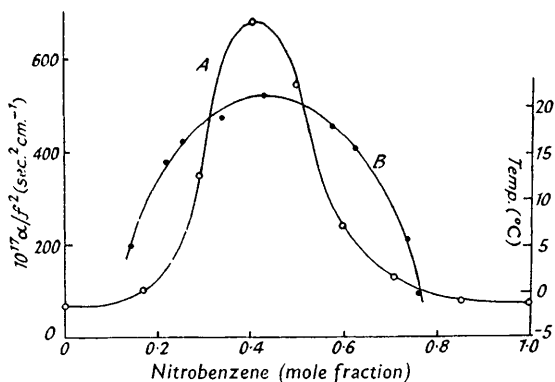


FIG. 14. Absorption in solutions of Type D; nitrobenzene in *n*-hexane. A, absorption at 25°; B, solubility.

[By courtesy of Sette, *Nuovo cim.*, 1955, **1**, 800.]

of the ultrasonic absorption in such mixtures is the persistence of the maximum absorption associated with the critical mixing phenomenon into the range of temperature far removed from the consolute temperature. The sound absorption is therefore sensitive to the existence of critical mixing even at temperatures more than 30° c removed from the critical conditions.

An important conclusion which can be drawn from the work on mixtures is that a completely satisfactory explanation of the behaviour can be found only if future experimental observations are extended to cover not only variations in temperature and concentration but also a frequency range sufficient to determine a substantial part of the relaxation.

The authors greatly appreciate the kindness of Dr. J. H. Andreae, Dr. A. A. Petrauskas, and Mr. M. S. de Groot for personal communications of their work which at the time of writing is awaiting publication.

²⁹ Maier and Mez, *Z. Naturforsch.*, 1952, **7a**, 300; 1955, **10a**, 997; Eppler, *ibid.*, p. 744.

³⁰ Sette, *Nuovo cim.*, 1955, **1**, 800.