441. *The* a priori *Calculation of Molecular Relaxation Times from the Shapes and Other Known Properties of Molecules.*

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Measurements are recorded of the relaxation times of nitrobenzene, 1-nitronaphthalene, 4-nitrodiphenyl, 9-nitroanthracene, benzophenone, fluorenone, pyridine, quinoline, *iso*quinoline, and acridine in a variety of solvents chosen from dioxan, *p*-xylene, carbon tetrachloride, benzene, toluene, *cyclo*hexane, *n*-heptane, and *n*-hexane. Equations are developed empirically, and tested against data from experiments, whereby τ may be computed *a priori* from shape or polarisability ellipsoids of the solute molecules, and the viscosities, depolarisation factors, and dielectric constants of the solvents.

Debye's treatment [1] of dielectric loss led to the well-known equation (1) for the relaxation time τ of a molecule of radius r in a medium having a coefficient of inner friction η_1^*:

$$\tau = 4\pi\eta_1^* r^3/kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As often used, with the macroscopic viscosity η_1 in place of the inaccessible η_1^*, and r^3 deduced from the molecular volume, eqn. (1) yields values of τ which may be 5—10 times those indicated by experiment. Two possible reasons for this are the non-equality of η_1^* and η_1 and the unreality of taking a sphere as a general model of all molecules. The former point has often been illustrated [2] and attention was early drawn to the latter by Perrin,[3] who suggested essentially the substitution of r^3 by the product of the three semi-axes of an ellipsoid. Perrin's idea has been elaborated by Fischer, Wirtz, and their collaborators,[4] while improved approximations to η_1^* have been suggested by Hill [5] and Hase; [6] these proposals will be considered later. At the outset our objective was the modification of eqn. (1) to improve its applicability to the *a priori* computation of the relaxation times of solutes at infinite dilution. Some recent success with the use of shape factors in related fields [7] encouraged the belief that they could be profitably introduced here. Accordingly the plan has been to determine τ for a standard molecule (nitrobenzene), in eight solvents, to attempt to fit it with certain properties of the media, and then to test the validities of any expressions so achieved on a variety of other solutes, 1-nitronaphthalene, 9-nitroanthracene, 4-nitrodiphenyl; and pyridine, quinoline, acridine, and *iso*quinoline, chosen for their obvious stereochemical relationships with nitrobenzene and pyridine.

Our results for relaxation times of nitrobenzene (10^{-12} sec.) were as follows (that for carbon disulphide is due to Whiffen [8]): Dioxan 21, *p*-xylene 14, carbon tetrachloride 14, benzene 11, toluene 11, carbon disulphide 8·6, *cyclo*hexane 9·3, *n*-heptane 6·4, *n*-hexane 6·8. These values appear in reasonable agreement with others, as follows (references in parentheses): Benzene 11·3 (10), 11·6 (11), 11·5 (12), 13·0 (13), 13·2 (14), 12·8 (8), 14·9 (6); carbon tetrachloride 15·2 (8), 19·6 (6); *cyclo*hexane 9·5 (8), 11·8 (6); *n*-hexane 8·5 (6); *n*-heptane 6·8 (8). (It should be mentioned that the measurements by Fischer *et al.* and

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[1] Debye, "Polar Molecules," Reinhold Publ. Corp., New York, 1929, Chap. V.

[2] *E.g.*, Various authors in "Dielectrics," *Trans. Faraday Soc.*, 1946, **42**, Appendix.

[3] Perrin, *J. Phys. Radium*, 1934, **5**, 497.

[4] (*a*) Budo, Fischer, and Miyamoto, *Physikal. Z.*, 1939, **40**, 337; (*b*) Fischer, *ibid.*, p. 645; (*c*) Fischer, *Z. Physik*, 1949, **127**, 49; (*d*) Spernol and Wirtz, *Z. Naturforsch.*, 1953, **8a**, 522; (*e*) Gierer and Wirtz, *ibid.*, p. 532.

[5] Hill, *Proc. Phys. Soc.*, 1954, **67**, *B*, 149.

[6] Hase, *Z. Naturforsch.*, 1953, **8a**, 695.

[7] Barclay and Le Fèvre, *J.*, 1950, 556; Holland and Le Fèvre, *ibid.*, p. 2166; Angyal, Barclay, and Le Fèvre, *ibid.*, p. 3370; Buckingham and Le Fèvre, *J.*, 1952, 1932; Le Fèvre, "Dipole Moments," Methuen, London 3rd edn., 1953, pp. 82, 83; Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 287.

[8] Whiffen, *Trans. Faraday Soc.*, 1950, **46**, 130.

TABLE 1. *Some properties of the solvents used.**

	$10^2\eta$ (P)	ε_{20}	Δ	V_{20} (c.c.)	$10^{24}r^3$ (c.c.)	$10^{25}\alpha_1$ (mean)
Dioxan	1·41	2·218	0·14	85·1	25·2	94·4
p-Xylene	0·64	2·270	0·63—0·64	123	36·4	141·2
CCl_4	0·97	2·238	0·048—0·056	96·6	28·6	105
C_6H_6	0·65	2·284	0·42—0·43	88·7	26·3	103·2
C_6H_5·Me	0·59	2·379	0·43—0·47	106	31·4	122·4
CS_2	0·37	2·641	0·64—0·68	60·2	17·8	83·45
cyclo-C_6H_{12}	0·97	2·023	0·063	108	32·0	108·7
C_7H_{16}	0·41	1·924	0·106	146	43·3	136·1
C_6H_{14}	0·32	1·890	0·087	130	38·5	117·8

For definition of symbols, see text. Viscosities, refractive indexes, and densities at 25° are from Timmermans, "Physicochemical constants of pure organic compounds," Elsevier, Amsterdam, 1950. Dielectric constants also therefrom and Maryott and Smith, "Table of dielectric constants of pure liquids," Nat. Bur. Stand. Circular 514, 1951. Depolarisation factors from Stuart, "Die Struktur des Freien Moleküls," Springer, Berlin, 1952, p. 356. Mean polarisabilities, α, calc. from R_D; $r = 0{\cdot}6667 \, . \, 10^{-8} \, V^{1/3}$ cm.

TABLE 2. *Dimensions and polarisabilities of solutes.*

	10^8A	10^8B	10^8C	$10^{24}ABC/8$	$10^{25}\alpha_{\text{mean}}$
$C_6H_5{\cdot}NO_2$	8·00	6·05	2·90	17·4	129
1-$NO_2{\cdot}C_{10}H_7$	8·00	8·70	2·90	25·2	197
9-$NO_2{\cdot}C_{14}H_9$	8·00	10·91	2·90	31·6	292
p-$NO_2{\cdot}C_6H_4{\cdot}$Ph	12·32	6·05	2·90	27·0 [a]	222
,, ...	12·32	6·05	6·05	56·4 [b]	222
C_5H_5N	6·1	6·2	2·9	13·7	91·3
C_9H_7N	6·1	8·7	2·9	19·3	156
iso-C_9H_7N	7·7	7·3	2·9	20·4	163
$C_{13}H_9N$	6·1	11·1	2·9	24·5	227

Rings are taken as [a] coplanar, [b] orthogonal.

TABLE 3. *Relaxation times* (10^{-12} *sec.*) *for nitrobenzene in various solvents.*

	Calc. from eqn.					Calc. from eqn.			
	(1)	(2)	(3)	Obs.*		(1)	(2)	(3)	Obs.*
Dioxan......	132	20	21	20—23	CS_2	35	8·0—8·4	8·2—8·6	8·6
p-Xylene...	60	15	15—16	13—14	*cyclo*-C_6H_4	91	13	14	9—12
CCl_4	91	13	13	13—20	*n*-C_7H_{16} ...	38	6·1	6·3	6·4
C_6H_6	61	12	13	11—15	*n*-C_6H_{14} ...	30	4·6	4·9	6·8—8·5
PhMe	55	11	11—12	11					

* Covering data from p. 2293.

Hase differ from the remainder in being made calorimetrically[9] at a wavelength of 3·4 m.) Correlations were sought between the values of τ given and many separate solvent properties, *e.g.*, adiabatic or isothermal compressibilities, and others considered earlier by Le Fèvre,[15] besides those collected in Table 1, from which it is evident that the relaxation does not follow viscosity, volume functions such as V_1/V_2, $\exp(-V_1/V_2)$, $\eta \exp(-V_1/V_2)$ etc., or others involving in a similar manner the polarisability ratios α_1/α_2. (For nitrobenzene at 20°: $V = 102$ c.c., $r^3 = 30{\cdot}2 \times 10^{-24}$ c.c., and $\alpha_{\text{mean}} = 129 \times 10^{-25}$ c.c.) By inspection it appeared that the products of the viscosities of Table 1 and some measure of the anisotropies of the solvents concerned would be more smoothly related with τ than are the viscosities themselves. Eventually it was found that $(\eta \exp \Delta)/(\varepsilon + 2)$ could be plotted fairly linearly against τ; here Δ is the depolarisation factor observed in (Rayleigh) scattered light from the liquid, ε the dielectric constant, and η a viscosity of the order of magnitude of a centipoise. Since Le Fèvre and Sullivan[16] had already noted a rough

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[9] Fischer and Frank, *Physikal. Z.*, 1939, **40**, 435.

[10] Henrion, quoted in ref. 7.

[11] Jackson and Powles, ref. 2, p. 101.

[12] Whiffen and Thompson, *ibid.*, p. 114.

[13] Cripwell and Sutherland, *ibid.*, p. 149.

[14] Fischer, *Z. Naturforsch.*, 1949, **4a**, 707.

[15] Le Fèvre, ref. 2, p. 162.

[16] Le Fèvre and Sullivan, *J.*, 1954, 2873.

correlation of τ with the mean polarisabilities and the shapes of solutes, the empirical equation (2) immediately followed:

$$\tau = 4\pi\eta_1\alpha_{\text{mean}}(\exp \Delta_1)(\exp h^2)^2/(\varepsilon_1 + 2)kT \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(h is defined by Holland and Le Fèvre.[7])

It happens that $(\alpha_{\text{mean}})(\exp h^2)^2$ is often numerically close to $ABC/8$ (A, B, and C are defined in ref. 7), *e.g.*, for nitrobenzene the values are $17{\cdot}00 \times 10^{-24}$ and $17{\cdot}40 \times 10^{-24}$ respectively. Equation (3) accordingly became an alternative to (2):

$$\tau = \pi\eta_1(\exp \Delta_1)ABC/2(\varepsilon_1 + 2)kT \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(In equations 1—3 the subscript 1 is used to distinguish solvent properties from those of the solute.) The applicability of equations (1), (2), and (3) to nitrobenzene as solute is shown as Table 3; the requisite quantities A, B, C, and α_{mean} are given in Table 2 together with data to be used later in this paper.

Predictions of τ based on equations (2) and (3) being in reasonable accord with values obtained by experiment, the work has been extended to cover seven other solutes (see Table 4).

TABLE 4. *Relaxation times* (10^{-12} *sec.*) *for other solutes in various solvents.*

	Calc. from eqn.		
Solvent	(2)	(3)	Obs.
	α-Nitronaphthalene		
Dioxan	32	30	23
p-Xylene	23	22	21
CCl_4	20	19	25
C_6H_6	19	18	20
PhMe	17—18	16—17	21
cyclo-C_6H_{12}	21	20	16
n-C_7H_{16}	9·7	9·1	14
n-C_6H_{14}	7·3	7·0	13
	9-Nitroanthracene		
p-Xylene	38—39	28	30
CCl_4	33	24	23
C_6H_6	32	23	28
n-C_7H_{14}	12	11	11
	Pyridine		
CCl_4	8·2—8·3	10	7·2
C_6H_6	7·9—8·0	10	4·4
n-C_7H_{44}	3·9	4·9	2·2

	Calc. from eqn.		
Solvent	(2)	(3)	Obs.
	Quinoline		
CCl_4	16	14—15	14
C_6H_6	15	14	10
n-C_7H_{14}	7·7	6·9	6·0
	iso*Quinoline*		
CCl_4	15	15—16	21
C_6H_6	15	14—15	15
n-C_7H_{14}	7·3	7·3	7·2
	Acridine		
CCl_4	28	18—19	26
C_6H_6	27	18	20

4-Nitrodiphenyl

	Calc. from eqn.			
	(2)[a]	(3)[b]	(3)[a]	Obs.
Dioxan	49	67	32	25
p-Xylene	35	49—50	24	23
CCl_4	31	42—43	20	21
C_6H_6	29	40—41	19—20	30

Rings are taken as [a] coplanar, [b] orthogonal.

Previous Empirical Approaches to the Problem.—Fischer,[4] starting from Perrin's idea[3] and elaborating his own earlier suggestions,[4a, b] proposed the equation: $\tau = 4\pi\eta fabc/4{\cdot}3kT$ in which a, b, and c are half-axes obtained similarly to our A, B, and C and f is a shape factor, dependent upon b/a and c/a (values are tabulated by Budó, Fischer, and Miyamoto[4a]), relating the τ of an ellipsoidal model to the τ of a sphere of equal volume. Applicability to measurements in benzene seems fairly good—values observed, as quoted in ref. 14 (in parentheses), follow those calculated (10^{-12} sec.): Me_2CO, 3·6 (3·3); $CHCl_3$, 7·0 (8·4); PhBr, 13 (12); $PhNO_2$, 11 (13). However, as Davies[17] has noted, "this apparently satisfactory . . . representation of the results is lost when the solvent is varied."

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[17] Davies, *Quart. Rev.*, 1954, **8**, 250.

More recently, instead of using a constant multiplier η (as was first done by Fischer[4b]), the needed coefficient of inner friction has been treated as a quantity dependent on *both* solute and solvent. Hase[6] puts $\eta_{\text{micro}} = \eta_{\text{macro}}$(function of V_2^*/V_1^*), where $V_1^* = 4\pi P_iQ_iR_i/3$, with P_i, Q_i, and R_i having the origin and significance of $A/2$, $B/2$, and $C/2$ (Table 2); asterisks are used to differentiate the V's from those, derived from densities and molecular weights, listed in Table 1. Hase accordingly writes $\tau = (3\eta f V_2^*/kT) \exp(-\Delta\, V_1^*/V_2^*)$, and from extant data on τ in a number of media deduces that α is a property of the solute molecule. His Table 8 however shows that it may lie between 0·4 and 2·5, and as α is apparently not predictable his equation cannot be used to provide τ *a priori*.

Wirtz and collaborators[4d, e] derive a "micro-friction factor" f_r of rotation, given by $f_{\text{rot.}} = [(6r_1/r_2) + (1 + r_1/r_2)^{-3}]^{-1}$ in which the radii r_1 and r_2 are obtained as $(0{\cdot}556V_i/\pi N)^{1/3}$ (where $V_i = M_i/d_i$). The relaxation time therefore becomes $\tau = 4\pi\eta r_2^{\,3} f_{\text{rot.}}/kT$. A test with nitrobenzene gives the following:

Solvent	(r_2/r_1) *	$\tau_{\text{calc.}}$	$\tau_{\text{obs.}}$	Solvent	(r_2/r_1) *	$\tau_{\text{calc.}}$	$\tau_{\text{obs.}}$
cyclo-C_6H_{12}	0·98	19	7·6—12	CS_2	1·19	8·9	8·6
C_6H_6	1·05	14	11—15	CCl_4	1·02	20	13—20

* From ref. 4*d*.

The agreement between $\tau_{\text{obs.}}$ and $\tau_{\text{calc.}}$ is slightly inferior to that displayed in Table 3, but r_2 cannot be evaluated for a dissolved solid. An analogous disability affects Hill's promising treatment[5] whereby τ = (function of moments of inertia and masses of the solvent and solute molecules) × ("mutual viscosity" of solvent and solute)/$2kT$. Unfortunately it appears necessary to know η_2 before the "mutual viscosity" can be computed.

Accordingly we claim that equations (2) and (3) have a wider usefulness than others suggested.

EXPERIMENTAL

Materials.—These were recrystallised or redistilled, as appropriate, and had the properties recorded for pure specimens; 9-nitroanthracene was obtained by direct nitration;[18] the heterocyclic bases were B.D.H. samples treated as set out in ref. 19.

Methods and Apparatus.—The equipment used was that of Le Fèvre and Sullivan[16] who gave dimensional details of the E_{010} cavity resonator involved, but deal only briefly with the general procedures of measurement. The following notes may therefore be useful.

The essential components (see Figure) are: (1) two 10 cm. oscillators, A and B built around CV-35 Klystrons, and containing voltage-regulated power supplies; in oscillator A two of the three brass slugs attached to the cavity of the Klystron are kept fixed, the remaining slug being insertable by a slow-motion fine control graduated over an arbitrary linear scale (readings on which are referred to as "frequency vernier settings"); (2) the cavity resonator described in ref. 16; (3) a crystal rectifier X, and galvanometer G, plus lamp and scale; (4) a quarter-wave co-axial cavity mixer; (5) a calibrated intermediate-frequency receiver readable to 0·01 Mc./sec. between 13·5 and 18·5 Mc./sec.; and (6) a calibrated co-axial line wave-meter (not shown).

TABLE 5. *Solvent constants additional to those listed by Le Fèvre and Sullivan.*[16]

$T°$ (K)	ε	d	D	$T°$ (K)	ε	d	D
	Dioxan				cyclo*Hexane*		
288	2·226	1·0392	8·337	288	2·031	0·7831	6·265
293	$2{\cdot}217_5$	1·0336	8·291	293	2·023	0·7785	6·228
	Toluene				n-*Hexane*		
288	2·403	0·8716	7·032	288	1·898	0·6639	5·315
293	2·391	0·8669	6·991	293	1·890	0·6594	5·279
	p-*Xylene*				n-*Heptane*		
288	2·278	0·8654	6·952	288	1·931	0·6878	5·504
293	2·270	0·8610	6·916	293	1·924	0·6837	5·472

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[18] Dimroth, *Ber.*, 1901, **34**, 221.

[19] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

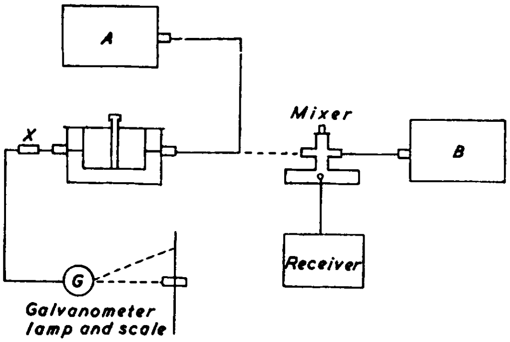
TABLE 6. *Dependence of incremental* tan δ *on concentration.*

Solvent	$10^5 w_2$	Δf (Mc./sec.)	$10^3 \Delta \tan \delta$
Solute: *Nitrobenzene*			
Dioxan	0	0·98	—
	211	2·30	5·27
	579	4·61	14·48
	0	1·18	—
	242	2·69	5·98
	396	3·65	9·82
p-Xylene	0	0·61	—
	246	1·60	3·93
	452	2·32	6·80
	537	2·75	8·51
	730	3·60	11·92
	847	3·97	13·33
CCl_4	0	0·65	—
	120	1·48	3·31
	273	2·52	7·45
	274	2·57	7·59
	336	2·98	9·26
	0	0·72	—
	377	3·24	10·04
	412	3·70	11·82
	0	0·62	—
	128	1·53	3·62
	262	2·49	7·44
Benzene	0	0·57	—
	356	1·71	4·55
	510	2·29	6·86
	756	3·04	9·85
	0	0·55	—
	205	1·18	2·51
	410	1·89	5·34
	708	2·81	9·01
	0	0·59	—
	249	1·39	3·19
	548	2·43	7·34
	845	3·46	11·45
Toluene	0	2·33	—
	410	3·57	4·91
	503	3·80	5·85
	683	4·30	7·84
	0	2·24	—
	419	3·38	4·55
	678	4·22	7·87
cyclo-C_6H_{12}	0	1·53	—
	1565	5·43	15·55
	2003	6·60	20·21
	2240	7·60	24·60
n-C_7H_{16}	0	0·80	—
	481	1·58	3·11
	761	2·02	4·86
	0	1·90	—
	632	1·90	4·15
	880	2·34	5·70
n-C_6H_{14}	0	0·62	—
	288	1·03	1·64
	580	1·54	3·67
	762	1·79	4·67
	0	0·59	—
	663	1·63	4·14
	1383	2·64	8·14
	1839	3·26	10·63
Solute : 1-*Nitronaphthalene*			
Dioxan	0	2·20	—
	787	6·13	15·67
	848	6·40	16·75
	1490	9·30	28·35
p-Xylene	0	0·80	—
	276	1·91	4·42
	305	1·97	4·66
	432	2·59	7·12
	0	0·86	—
	171	1·57	2·84
CCl_4	0	0·61	—
	103	1·45	3·35
	155	1·87	5·03
	256	2·80	8·70
C_6H_6	0	0·63	—
	403	2·12	5·94
	541	2·66	8·10
	553	2·65	8·06
	604	2·88	8·97
	740	3·41	11·09
	0	0·65	—
	396	2·17	6·06
	555	2·82	8·65
PhMe	0	2·04	—
	208	2·81	3·06
	398	3·49	5·76
	0	2·23	—
	338	3·47	5·32
	424	3·90	6·57
cyclo-C_6H_{12}	0	0·63	—
	386	1·76	4·49
	456	2·02	5·42
	682	2·60	7·84
n-C_7H_{16}	0	0·81	—
	483	1·81	3·99
	903	2·66	7·37
	0	0·77	—
	524	1·87	4·38
	885	2·59	7·25
n-C_6H_{14}	0	0·61	—
	342	1·30	2·74
	386	1·41	3·19
	522	1·70	4·33
Solute : 4-*Nitrodiphenyl*			
Dioxan	0	2·08	—
	231	3·22	4·54
	292	3·54	5·82
	309	3·70	6·46
p-Xylene	0	0·75	—
	316	2·19	5·75
	466	2·78	8·09
	0	0·70	—
	137	1·42	2·90
	446	2·64	7·72
CCl_4	0	1·63	—
	410	4·80	12·64
	414	49·4	13·19
	463	5·24	14·38
	0	1·61	—
	287	3·79	8·69
	437	5·08	13·83
	493	5·24	14·47
C_6H_6	0	0·64	—
	250	1·90	5·02
	331	2·30	6·60
	649	3·88	12·96
	0	0·57	—
	277	1·95	5·50
	421	1·65	8·30
	721	4·17	14·36
	0	0·66	—
	168	1·49	3·31
	263	1·99	5·31

TABLE 6. (*Continued.*)

Solvent	$10^5 w_2$	Δf (Mc./sec.)	$10^3 \Delta \tan \delta$
Solute: 9-*Nitroanthracene*			
p-Xylene ……	0	1·79	—
	230	2·51	2·77
	498	3·21	5·59
	530	3·27	5·70
	671	3·69	7·32
	1216	5·32	13·62
CCl_4 …………	0	1·79	—
	149	2·58	3·05
	219	3·00	4·67
	341	3·68	7·28
C_6H_6 …………	0	1·52	—
	275	2·30	3·12
	566	3·18	6·28
	836	3·97	9·46
n-C_7H_{16} ………	0	1·82	—
	134	1·92	0·54
	168	2·01	0·73
	242	2·11	1·12
	307	2·21	1·46
	321	2·25	1·66
Solute: *Benzophenone*			
C_6H_6 …………	0	1·80	—
	655	2·87	4·27
	684	2·90	4·36
	700	2·94	4·54
	780	2·95	4·59
	802	3·01	4·82
	902	3·10	5·22
	911	3·30	5·97
	1165	3·72	7·65
Solute: *Fluorenone*			
C_6H_6 …………	0	1·52	—
	694	3·07	6·18
	714	3·11	6·34
	1006	3·79	9·05
	0	1·58	—
	699	3·14	6·22
	725	3·15	6·26
	1153	4·03	9·77
	0	1·65	—
	781	3·41	7·01
	966	3·77	8·44
Solute: *Pyridine*			
CCl_4 …………	0	1·24	—
	204	2·06	3·16
	595	2·68	5·56
	633	2·76	5·86
	0	1·57	—
	613	3·03	5·63
	931	3·35	6·86
	1221	4·20	10·14
	0	1·74	—
	2049	5·20	13·36
	2664	6·34	16·06
C_6H_6 …………	0	1·64	—
	914	2·22	2·25
	0	1·67	—
	1813	2·84	4·51
	2235	3·18	5·83
	2376	3·46	6·91
n-C_7H_{16} ………	0	1·81	—
	869	1·98	0·672
	871	2·05	0·936
	964	2·06	0·972
	0	1·71	—
Solute: *Pyridine*			
n-C_7H_{16} ………	1900	2·20	1·88
	2013	2·25	2·08
	2236	2·40	2·66
Solute: *Quinoline*			
CCl_4 …………	0	1·80	—
	537	2·95	4·44
	620	3·65	7·14
	0	1·88	—
	590	3·29	5·44
	679	3·52	6·32
	787	3·76	7·25
C_6H_6 …………	0	1·71	—
	745	2·41	2·66
	1025	2·66	3·62
	1326	3·09	5·29
	0	1·79	—
	754	2·51	2·77
	908	2·73	3·63
	1471	3·10	5·03
n-C_7H_{16} ………	0	1·62	—
	1713	2·26	2·47
	2044	2·45	3·20
	2392	2·76	4·39
Solute: iso*Quinoline*			
CCl_4 …………	0	1·80	—
	446	3·85	7·91
	769	4·55	10·61
	917	5·62	14·74
	0	1·20	—
	1924	10·1	34·34
	2013	10·5	35·88
	2254	11·1	38·20
C_6H_6 …………	0	1·67	—
	664	2·90	4·74
	679	2·92	4·82
	1273	3·84	8·34
	0	1·69	—
	1277	4·13	9·42
	1489	4·59	11·20
	1772	4·87	12·28
n-C_7H_{16} ………	0	1·63	—
	1376	2·58	3·67
	1442	2·68	4·06
	2196	3·29	6·41
Solute: *Acridine*			
CCl_4 …………	0	1·86	—
	186	2·35	1·90
	425	3·05	4·60
	779	3·74	7·26
	0	1·76	—
	813	3·75	7·68
	840	4·00	8·64
	963	4·30	9·80
	0	1·70	—
	759	3·67	7·60
	1055	4·55	11·00
C_6H_6 …………	0	1·68	—
	889	2·73	4·06
	935	2·75	4·13
	1558	3·53	7·14
	0	1·70	—
	1306	3·12	5·47
	1626	3·56	7·18
	1708	3·75	7·91

Both oscillators and the receiver are run for 1 hr. to reach frequency stability; meanwhile the resonator (kept in a desiccator when not in use) is polished with a soft cloth, and a series of solutions made up. The most concentrated solution is put into the quartz tube[16] so that its level is above the resonator lid. The frequency of *A* is then varied across the point of resonance, galvanometer deflections against frequency vernier settings being recorded. From the resulting plot the frequency vernier settings corresponding to the maximum and the two half-heights on each side of the maximum are obtained (f_r, $f_{y/2}'$ and $f_{y/2}''$ respectively).



The vernier is now reset on f_r and the coaxial cable from *A* connected to the wave-meter (instead of the resonator). This gives f_r directly (it is always *ca.* 3109 Mc./sec.). Next, with the vernier at $f_y/_2'$, the cable from *A* is joined to the mixer (broken line in Figure) so that the output from *A* combines with that from *B*, which is adjusted until a beat-note starts to be

TABLE 7. *Calculation of observed relaxation times.*

Solvent	μ (D) *	ψ_{mean}	Temp.	$10^{12}\tau$ (sec.)
		Nitrobenzene		
Dioxan ...	3·910	2·49	295°	21
p-Xylene...	3·917	1·57	290	14
CCl_4	3·925	2·84	295	14
C_6H_6	3·967	1·31	298	11
PhMe	3·83	1·15	295	11
cyclo-C_6H_{12}	3·972	1·00	388	9·3
n-C_7H_{16} ...	4·10	0·65	288	6·4
n-C_6H_4 ...	4·038	0·62	298	6·8
		1-*Nitronaphthalene*		
Dioxan ...	3·90	1·94	288	23
p-Xylene...	(4·0)	1·61	389	21
CCl_4	4·00	3·32	290	25
C_6H_6	3·98	1·50	298	20
PhMe	3·87	1·53	289	21
cyclo-C_6H_{12}	(4·0)	1·16	290	16
n-C_7H_{16} ...	(4·0)	0·82	290	14
n-C_6H_{14} ...	(4·0)	0·82	290	13
		4-*Nitrodiphenyl*		
Dioxan ...	4·16	2·02	288	25
p-Xylene...	(4·4)	1·77	288	23
CCl_4	$4·39_5$	3·09	290	21
C_6H_6	4·36	1·99	298	30
		9-*Nitroanthracene*		
p-Xylene...	(3·4)	1·11	288	30
CCl_4	3·71	2·12	287	23
C_6H_6	3·43	1·12	285	28
n-C_7H_{14} ...	(3·7)	0·47	286	11
		Benzophenone		
C_6H_6	2·7	0·63	298	19·2 (or 136)
		Fluorenone		
C_6H_6	3·35	0·88	298	17·0 (or 156)
		Pyridine		
CCl_4	2·37	0·88	288	7·2
C_6H_6	2·25	0·27	286	4·4
n-C_7H_{16} ...	2·27	0·10	287	2·2
		Quinoline		
CCl_4	2·27	0·95	288	14
C_6H_6	2·24	0·37	287	10
n-C_7H_{16} ...	2·17	0·16	287	6·0
		iso*Quinoline*		
CCl_4	2·65	1·70	288	21
C_6H_6	2·61	0·71	286	15
n-C_7H_{16} ...	2·60	0·28	287	7·2
		Acridine		
CCl_4	2·22	1·01	288	26
C_6H_6	2·18	0·45	287	20

* Dipole moments for nitrobenzene are from Smith and Cleverdon (*Trans. Faraday Soc.*, 1949, **45**, 109) when shown as four figures, otherwise from the M.I.T. Tables. Remaining data come from the following paper or from refs. 19 and 20. Values in parentheses are assumed.

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[20] Hughes, Le Fèvre, and Le Fèvre, *J.*, 1937, 202.

heard in the loud speaker. The mixer is then tuned until the signal is a maximum. The receiver dial reading is then noted. A repetition with the frequency vernier of A at $f_{y/2}''$ then gives another receiver reading, the difference of which from the first is the desired Δf. The Q factor of the system is $f_r/\Delta f$. The same procedure is followed for the other solutions, and for the solvent. Then we have :

$$\Delta \tan \delta = (\text{constant})(1/Q_{12} - 1/Q_1)$$

where the constant may be determined from the geometry of the resonator, or more conveniently, from a series of measurements on liquids or solutions having known values of $\Delta \tan \delta$. Subsequent computation is based upon equation (5) of ref. 16, ψ being a mean obtained as $\Sigma(\Delta \tan \delta/\Sigma w_2)$. Solvent constants ($D$ in ref. 16) appropriate for the temperature range commonly experienced are given in Table 5 for those media not listed by Le Fèvre and Sullivan;[16] Table 6 records the experimental quantities requisite to secure the values of ψ, and Table 7 presents the relaxation times now found.

Tables 6 and 7 include data for benzophenone. This solute was chosen as a " standard " because its relaxation time has been measured at different frequencies and temperatures; in benzene τ undoubtedly lies [2, 14] between 16 and 21 × 10^{-12} sec. Now by the nature of equation 5 given by Le Fèvre and Sullivan [16] τ is extracted from observations as a pair of values, one high and one low. As we lacked equipment working at a second wavelength we could not select τ by experiment directly in cases where the larger τ might have been correct (*e.g.*, with 4-nitrodiphenyl). Accordingly τ for benzophenone emerged as 19 or 136 × 10^{-16} sec.—a pair of values resembling in magnitude those experienced with several other of the larger solutes. Since the lower figure is appropriate for benzophenone we assumed the same to be true in the remaining doubtful instances; Tables 4 and 7 have been compiled on this basis.

Fluorenone was added for interest: its aromatic rings [20] must be held rigidly in contrast to those of benzophenone; this important structural difference does not seriously affect the observed relaxation times.

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