

The Hydrolysis of the Methyl Halides

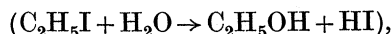
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An assumption common to the many current theories of chemical kinetics is that the velocity (k) of reaction is proportional to the Maxwell-Boltzmann factor $e^{-E/RT}$, which in simple cases represents the fractional number of molecules possessing an amount of internal energy not less than E . The condition that reacting molecules must possess a critical energy in excess of the average value for all the molecules is, however, only one from a number of conditions which must in general be fulfilled before chemical change can take place. The present development of the subject calls for quantitative information concerning these conditions, which have hitherto been discussed almost exclusively from the theoretical standpoint.

When the complete expression for the velocity of reaction contains temperature-variable terms other than the Maxwell-Boltzmann factor, it is clear that the Arrhenius energy of activation (E_A), defined by the relation $E_A = RT^2 \frac{\partial \ln k}{\partial T}$, cannot be constant. To determine its variation with temperature requires, however, data of higher accuracy than those usually available; and our experimental knowledge on the problem is still meagre. Perhaps the best example is the inversion of cane sugar, for which it has been found that $\frac{\partial E_A}{\partial T} = -98 \pm 4$ (Moelwyn-Hughes 1934). Values of the same order of magnitude must prevail also for disaccharides generally (Moelwyn-Hughes 1928). An important consequence of these results is that the true energy of activation is at least twice as great as the familiar but erroneous figures generally accepted, and that the corresponding Maxwell-Boltzmann factor in the expression for the velocity is incomparably less than one had imagined.

The glycosides—particularly sucrose—are complicated structures, which, moreover, hydrolyse only in the presence of catalysts; and the questions arise as to how far high values of $-\partial E_A/\partial T$ are specific to changes suffered by large^{*} molecules, or to catalysis. The experimental investigation of the uncatalysed hydrolysis of a suitable and simple molecule should allow of a decision. Ethyl iodide presented itself as a favourable case



but its study is complicated by a side reaction ($\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$) which is responsible for severe if only occasional explosions; and the work, for this reason and for others, was abandoned (Moelwyn-Hughes 1933).

We here describe experiments on the uncatalysed hydrolysis of three methyl halides, which we have found to be free from complications, and to proceed unimolecularly to completion at all accessible concentrations and temperatures. The results in condensed form are shown in Table I, with energies in calories per gram-molecule, and velocity constants in reciprocal seconds. These figures show beyond doubt that high values of $-\partial E_A/\partial T$ are not specific to the catalysed hydrolysis of glycosides, but hold also for the uncatalysed hydrolysis of methyl halides. In both cases the values of $-\partial E_A/\partial T$ are of a higher order of magnitude than those found for reactions occurring between ions and polar molecules (Moelwyn-Hughes 1936*a*).

TABLE I

	CH_3Cl	CH_3Br	CH_3I
$k_{298.1}$	1.99×10^{-8}	3.57×10^{-7}	6.87×10^{-8}
$k_{373.1}$	1.08×10^{-4}	1.31×10^{-3}	4.47×10^{-4}
$E_{298.1}$	27,703	26,525	28,147
$E_{373.1}$	22,706	21,424	23,111
$\partial E_A/\partial T$	-66.62	-68.01	-67.14

It is too early yet to generalize, but we may say that a marked fall in the apparent energy of activation with rise in temperature characterizes both simple and complicated hydrolyses for which most accurate data are available.

EXPERIMENTAL METHOD

Fig. 1 illustrates the apparatus used for preparing the solutions. Ordinary distilled water, which separate experiments showed to be as suitable as the purest conductivity water, is sucked into the 500 c.c. bulb *A*, where it is vigorously boiled at 20° C. The vapour of the methyl halide, stored in the 3-litre bulb *B*, is led over anhydrous calcium chloride into the water in *A*, where it is allowed to bubble slowly for a day or two, pending saturation. After measuring the partial pressure of the methyl halide, the solution is delivered into graduated reaction vessels by letting in air gently and at equal rates to both limbs of the bubbler; agitation of the solution leads to loss of solute vapour—a difficulty responsible for some of the irregularities found in previous work (Moelwyn-Hughes 1933). The sealed tubes are placed separately in pairs of concentric metal cylinders of the type described by Moelwyn-Hughes and Hinshelwood (1931). After

immersion for a measured time in electrically regulated or in boiling-vapour thermostats, the contents of each tube are analysed for halide and hydrogen ions and for free halogen. The end-point of each run corresponds to complete hydrolysis according to the equation

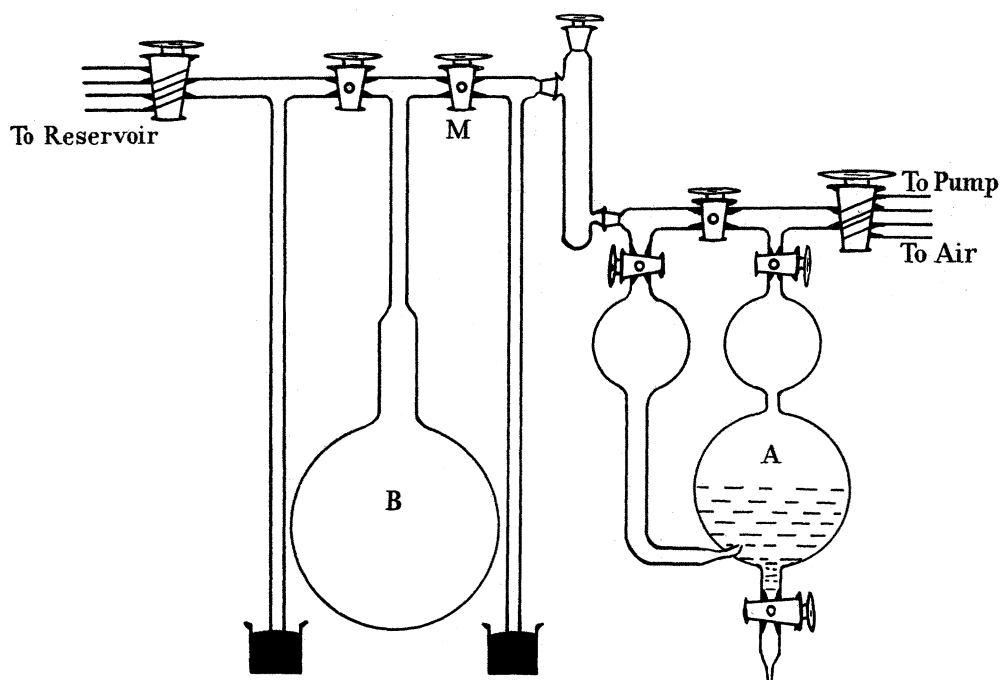


FIG. 1

Due, however, to an inevitable escape of some solute vapour, the first tube of a series to be filled usually required rather more analytical reagent than the last, but the loss seldom exceeded 1%, and, as shown in Table II, was less in favourable circumstances.

TABLE II—STANDARD REAGENT (C.C.) FOR REPRESENTATIVE
END-POINT TITRATIONS

	CH_3Cl	CH_3Br	CH_3I
First tube filled	39.38	10.45	42.43
Last tube filled	38.90	10.38	42.12
First	67.40	24.96	43.84
Last	67.14	24.84	33.74
First	93.37	108.55	51.61
Last	92.43	108.50	51.58

That the end-points correspond to complete hydrolysis was shown by treating the hydrolysed solutions with alcoholic potash or with aqueous silver nitrate, when no further change could be detected. Previous work (1933) traced the formation of some free halogen—not exceeding 1%—quantitatively to atmospheric oxidation, hence in the present work no precautions were taken to exclude oxygen from the vapour above the solutions in the sealed tubes. In the case of methyl iodide, a tared solution made up to 0.3118*N* gave on analysis 0.3071*N* iodide, or 98.5%; and 0.88% molecular iodine. In the case of the other halides, the amount of free halogen formed was even less, and was ignored. The methyl halides, supplied by Kahlbaum, were found to be free from acid and uncombined halogen.

STATIC MEASUREMENTS

The distribution of methyl chloride and methyl bromide between the vapour phase and an aqueous solution was determined at 20° C., the particulars of a given experiment being as follows. Bulb *A* containing water

TABLE III—DISTRIBUTION OF METHYL CHLORIDE AT 293.1° BETWEEN THE VAPOUR PHASE AND AN AQUEOUS SOLUTION

Partial pressure in the vapour phase (mm. Hg)	Concentration in solution (mmol./litre)	<i>p/c</i>
25.5	2.36	10.8
108.3	10.74	10.1
183	17.68	10.35
259.5	25.31	10.25
354	33.4	10.6
432.5	41.25	10.5
480	46.1	10.4

Average = 10.4

saturated with methyl chloride had a total pressure of 278.5 mm. Hg. Subtracting the vapour pressure of pure water (17.5 mm.) and the hydrostatic pressure (1.5 mm.) due to a head of 2 cm. of water, the partial pressure, *p*, of methyl chloride in the gas phase is 278.5 – 19.0 = 259.5 mm., assuming Dalton's law. The first tube of 20 c.c. required, after hydrolysis, 44.75 c.c. of 0.0114*N* sodium hydroxide to neutralize the acid generated; and the last tube required 44.05 c.c. Hence the concentration of solute is 25.31 mmol. per litre, and the distribution ratio (*p/c*) is 10.25 in these units. Other values found are reproduced in Tables III and IV. Occasionally, at the lower

pressures, high values of this coefficient were found, but repetition showed the tabulated figures to be correct, and the discrepancy to be due to loss of vapour, which has a relatively greater effect under these circumstances. Within the region of pressures examined, Henry's law is obeyed. Converting the concentrations in both phases to molecular units, we have $c_{\text{Solution}}/c_{\text{Vapour}} = 0.600$ in the case of methyl chloride, and 1.315 in the case of methyl bromide. The corresponding energy terms,

$$w = RT \ln (c_{\text{Solution}}/c_{\text{Gas}}),$$

are -297 and $+159$ respectively. These figures, while being useful for the kinetic purpose for which they were obtained, have no thermodynamic significance as they do not refer to equilibria.

TABLE IV—DISTRIBUTION OF METHYL BROMIDE AT 293.1° BETWEEN THE VAPOUR PHASE AND AN AQUEOUS SOLUTION

p	c	p/c
42	8.85	4.75
210	43.9	4.78
335	70.7	4.74
350	73.2	4.78
472	99.9	4.73
497	104.2	4.77
498	104.5	4.76

Average = 4.76

KINETIC MEASUREMENTS

Unimolecular velocity coefficients were determined by the usual methods from the equation

$$k = \frac{1}{t_2 - t_1} \ln \frac{T_{\infty} - T_1}{T_{\infty} - T_2},$$

where T stands for the titre at time t sec. Determination of halide by Volhard's method, using standard silver nitrate and potassium thiocyanate with ferric alum as indicator, gave results in agreement with estimates of acidity using litmus. For example, Exp. 12 of the methyl bromide series gave $k = 1.84_0 \times 10^{-4}$ sec. $^{-1}$ by the first method, while Exp. 2 performed some weeks previously at the same temperature gave $1.83_4 \times 10^{-4}$ by the second method. The two procedures were adopted indiscriminately, except in the case of methyl chloride, where the estimation of hydrogen ion is less laborious than the other. Some specimen results are shown in Tables V, VI and VII. The positive titre for $t = 0$ in Table V indicates some delay

TABLE V—METHYL CHLORIDE IN WATER AT 357.30°

<i>t</i> min.	<i>T</i> , c.c. 0.00950 <i>N</i> NaOH per 20 c.c. sample	<i>k</i> × 10 ⁵ sec. ⁻¹
0	0.22	—
50	5.00	2.74
134	11.04	2.70
180	13.74	2.76
288	20.81	2.70
420	27.86	2.75
560	33.20	2.70
830	40.77	2.65
∞	55.53	—
Average		2.71
Duplicate		2.67
		$k = 2.69 \times 10^{-5}$

TABLE VI—METHYL BROMIDE IN WATER AT 330.70°

<i>t</i> min.	<i>T</i> , c.c. 0.02020 <i>N</i> AgNO ₃ per 10 c.c. sample	<i>k</i> × 10 ⁴ sec. ⁻¹
0	0	—
35	2.43	2.43
88	5.92	2.46
109	7.13	2.43
140	9.11	2.48
256	15.42	2.49
300	17.30	2.45
412	22.08	2.46
482	24.75	2.47
∞	49.49	—
Average		2.46
Duplicate		2.48
		$k = 2.47 \times 10^{-4}$

TABLE VII—METHYL IODIDE IN WATER AT 321.23°

<i>t</i> min.	<i>T</i> , c.c. 0.02018 <i>N</i> AgNO ₃ per 20 c.c. sample	<i>k</i> × 10 ⁶ sec. ⁻¹
0	0	—
524	2.48	1.95
865	4.08	1.94
1475	6.83	1.95
1953	9.00	1.99
2770	12.03	1.96
2932	12.85	2.00
2735	15.22	1.93
∞	43.62	—
Average		1.96
Duplicate		1.90
		$k = 1.93 \times 10^{-6}$

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between charging the tubes and starting the run. Results to be described in the following paragraph suggest the possibility of a slight variation in k during the course of a single experiment. No such change could, however, be detected; where drifts occurred, they were as often upwards as downwards, and are probably due to experimental error.

THE DILUTION EFFECT

The extent to which the rate of hydrolysis is influenced by the dilution is illustrated in Table VIII, where the initial concentration of methyl bromide has been varied ninefold, which is the limit attainable by the present apparatus and technique.

TABLE VIII—THE VARIATION OF k WITH DILUTION

T ° abs.	Initial concentration of methyl bromide g.-mol./litre	$k \times 10^4$ sec. ⁻¹
363.40 \pm 0.06	0.0122	5.28 \pm 0.10
363.33 \pm 0.06	0.0303	5.58 \pm 0.08
363.12 \pm 0.04	0.1045	6.06 \pm 0.10

The reaction was in each case followed until at least 75% of the total change. The results are approximately expressible by a square-root law ($k \times 10^4 = 5.00 + 3.3c^{\frac{1}{2}}$), but supplementary evidence points to a limiting velocity constant for the saturated solution. The results leave no doubt as to the kinetic order of reaction.

THE INFLUENCE OF TEMPERATURE

With a fixed initial concentration of solute, the velocity of hydrolysis has been determined over a temperature range sufficient, in each case, to alter the rate by a factor of at least one thousand. The results do not conform with an equation of the Arrhenius type, but may be represented, as shown in Tables IX, X and XI, by the following formulae:

$$\text{Methyl chloride: } \log_{10} k = 110.223 - \frac{10,403}{T} - 33.559 \log_{10} T;$$

$$\text{Methyl bromide: } \log_{10} k = 112.656 - \frac{10,236}{T} - 34.259 \log_{10} T;$$

$$\text{Methyl iodide: } \log_{10} k = 111.859 - \frac{10,534}{T} - 33.821 \log_{10} T.$$

These expressions are valid as first approximations, and have been used to obtain the values of E_A and $\partial E_A/\partial T$ given in Table I. The most accurate set of data refer to methyl bromide, on account of its relatively great solubility. Detailed analysis of all the results suggest that $-\partial E_A/\partial T$ passes through a maximum within the experimental temperature region, but from

TABLE IX—METHYL CHLORIDE (0.0376 N)

T	k_{observed}	k_{formula}
314.78	2.30×10^{-7}	2.21×10^{-7}
326.24	9.58×10^{-7}	9.60×10^{-7}
333.11	2.16×10^{-6}	2.18×10^{-6}
341.28	5.43×10^{-6}	5.40×10^{-6}
348.99	1.22×10^{-5}	1.20×10^{-5}
357.30	2.69×10^{-5}	2.70×10^{-5}
373.37	1.08×10^{-4}	1.10×10^{-4}
383.98	2.48×10^{-4}	2.54×10^{-4}

TABLE X—METHYL BROMIDE (0.0949 N)

T	k_{observed}	k_{formula}
290.13	1.07×10^{-7}	1.04×10^{-7}
308.83	1.65×10^{-6}	1.65×10^{-6}
319.50	6.71×10^{-6}	6.57×10^{-6}
330.70	2.47×10^{-5}	2.46×10^{-5}
335.02	3.91×10^{-5}	3.94×10^{-5}
350.27	1.84×10^{-4}	1.84×10^{-4}
363.38	6.06×10^{-4}	6.12×10^{-4}
373.18	1.28×10^{-3}	1.31×10^{-3}

TABLE XI—METHYL IODIDE (0.0467 N)

T	k_{observed}	k_{formula}
308.87	3.43×10^{-7}	3.53×10^{-7}
321.23	1.93×10^{-6}	1.92×10^{-6}
323.69	2.70×10^{-6}	2.64×10^{-6}
328.72	4.81×10^{-6}	4.925×10^{-6}
333.88	8.72×10^{-6}	9.08×10^{-6}
342.92	2.49×10^{-5}	2.50×10^{-5}
363.06	1.80×10^{-4}	1.84×10^{-4}
372.92	4.31×10^{-4}	4.34×10^{-4}

the form of the above empirical equations, the second differential coefficient of E_A with respect to temperature cannot be estimated with accuracy. The last numerical constant in these expressions (and consequently $\partial E_A/\partial T$) is to be regarded as the average value for the explored temperature interval. In the case of methyl bromide, it varies from the actual values in the different temperature regions by about $\pm 10\%$ of the mean value. The variations in the other cases are higher.

DISCUSSION

The principal feature of these results is that the temperature coefficient of the apparent energy of activation is as great as -67 for the most simple cases of uncatalysed hydrolyses hitherto investigated. No single theory yet advanced can consistently account for this magnitude, and it appears that many of the hypotheses independently furthered in various directions must be co-ordinated to furnish a satisfactory solution of the problem. Before briefly referring to these, we may make some inferences as to the mechanism of hydrolysis on the basis of the present experimental facts.

The methyl halide molecule is capable of nine internal motions, most of which, from the known molecular frequencies, are fairly stiff vibrations, incapable at ordinary temperatures of contributing appreciably to the specific heat term. To explain the present observations we must consequently look to certain extramolecular effects, such as the rotation of the solute molecule as a whole in its solvent envelope, or to the weak vibrations which characterize the solute-solvent contacts. The measurable step in hydrolysis requires the participation of many bonds, exceeding in number those which are found within a single solute molecule. The reaction is thus a multimolecular one, although there is no objection to regarding it as the unimolecular decomposition of a cluster of solvent molecules with a solute molecule at the centre. The conclusion tallies well with the fact that the products of reaction are solvated ions with a pseudocrystalline structure. The halide ion retains this structure, but the methyl ion replaces a hydrogen ion from a water molecule.

The decomposition of the alkyl halides in the gaseous phase (Vernon and Daniels 1932) requires a greater apparent energy of activation than the true energy of activation (*ca.* 48,000) for the hydrolysis. The difference is great enough to render improbable, though not to exclude, the mechanism of a rate-determining formation of free radicals in solution, followed by rapid polar changes, including ionic solvation.

Another mechanism, provisionally ignored pending further work, is the simultaneous approach of a hydroxyl ion and a hydrogen ion from opposite sides of the methyl halide molecule (*cf.* Ogg and Polanyi 1935; Moelwyn-Hughes 1936*b*).

Accepting the rate-determining step to be the simultaneous attack of the solute molecule by many of the solvent molecules which surround it, we may note three effects which can contribute to the fall in the Arrhenius energy of activation. (1) Let some of the energy reside in a number, F , of bonds which are assumed to oscillate classically and to be feebly coupled;

then $E_A = \text{constant} - F \cdot RT$ (Hinshelwood 1926; Fowler and Rideal 1927). It is improbable that the whole of the observed effect is due to this distribution of energy; if it were, the activated cluster would have an average life of 1 sec. (when $F = 34$, $T = 373.1$, $E = 47,600$; activated fraction $= 1.86 \times 10^{-4}$). Moreover, in cases such as the inversion of cane-sugar ($F = 49$, $E = 58,200$, $T = 298.1$; activated fraction $= 1.74 \times 10^{-7}$), the supply of activated complexes is barely sufficient to maintain a stationary concentration. It seems evident, however, that the distribution of the activation energy among a number of degrees of freedom accounts for some of the observed effect, and yields a theoretical expression which is formally compatible with experiment. This opens up the question of how far the actual motions resulting from the interaction of solute and solvent molecules may be treated as classical oscillations. (2) Let the solute and solvent molecules have electrical moments of magnitude μ_A and μ_s respectively, and an average separation \bar{r}_0 . Assuming the critical separation, which differs from \bar{r}_0 , to be independent of temperature, and considering one solute molecule to make contact with x solvent molecules, we have

$$E_A = \text{constant} + \frac{x\mu_A\mu_s}{\bar{r}_0^3} \left\{ 1 + 3 \left(\frac{\partial \ln \bar{r}_0}{\partial \ln T} \right)_p \right\} \quad (\text{Moelwyn-Hughes 1937}).$$

Hence the existence of dipole-dipole attractions also partly accounts for the observed fall in the Arrhenius constant, though the motion implied cannot be a simple harmonic one. (3) The acquisition and appropriate distribution of internal energy by the reacting cluster and the adjustment of potential energy are not the only conditions which must be fulfilled before chemical change can take place. The internally activated solute molecule must turn round in the sheath of solvent molecules to find a position which, from the purely steric as well as from the potential-energy consideration, is most favourable to reaction. To do so entails the expenditure of energy, which varies with the temperature, and may be estimated from the average speed of rotation of a solute molecule. Using Einstein's expression for a spherical molecule of radius r in a medium of viscosity η , we have $\bar{v} = kT/4\pi r^3\eta$. This effect accounts for a partial $\partial E_A/\partial T$ of about -15 .

Not one of the three expressions discussed here can be regarded as quantitatively applicable to the systems under investigation, but they all indicate directions along which further progress may be sought.

The average decrease in molecular heat attending the dissociation of fifteen electrolytes, chiefly acids and bases, in aqueous solution at 298.1° is -38.8 . The reverse process, i.e. the combination of ions to form un-

dissociated molecules, is known to be accompanied by much smaller specific heat changes, hence the ionization of electrolytes in water may be included, along with the hydrolysis of glycosides and alkyl halides, in that category of chemical changes for which the equation of Arrhenius is not applicable. These examples are experimentally more reliable than the dubious instances cited by La Mer (1933), with whose theoretical treatment, however, we are in agreement. While this work was in progress, two further instances have come to light of reactions which probably belong to this category. They are the mutarotation of glucose, for which $\partial E_A/\partial T = -27.0 \pm 1.6$ (Smith and Smith 1937), and the decomposition of oxalic acid in water, for which a much higher value holds (Dinglinger and Schroer 1937). It is rather surprising that no such effect has yet been detected in the numerous hydrolyses and alcoholyses of the substituted methyl halides (e.g. Dawson and Pycock 1936; Hughes and Ingold 1937). Though $\partial E_A/\partial T$ in solvents other than water may well be relatively small, the "fall effect" must be regarded in these instances as unrevealed rather than absent.

As far as we are able to generalize, we may say that: (1) The inapplicability of the Arrhenius equation is most marked in reactions involving solute and solvent. These reactions have for some time been regarded as somewhat special cases, requiring a modification of the Arrhenius law (Moelwyn-Hughes 1933), hence the present discoveries, while demanding an adjustment of ideas, need not distort the general presentation of the kinetics of reactions in solution. (2) The temperature coefficient of the apparent energy of activation is always negative in the regions explored.

The present work was carried out in collaboration with Professor E. K. Rideal, F.R.S., for whose advice and guidance I am once more greatly indebted.

SUMMARY

For a chemical reaction proceeding with measurable rate, the most significant single constant is the energy of activation, found by the familiar method of Arrhenius. The value obtained is, in the majority of known cases, a true constant over the accessible temperature regions. In the case of the catalysed hydrolysis of some complicated molecules, namely the glycosides, it has, however, been found (1934) that the energy of activation falls markedly with a rise in temperature. As the result carried significant theoretical consequences, it became necessary to give an experimental answer to the question as to whether this fall was specific to the acidic hydrolyses of glycosides, or of a more general character. In the present

work, we have investigated the uncatalysed and uncomplicated hydrolysis of some very simple molecules, namely the methyl halides, and have found that in these cases also the Arrhenius constant falls as the temperature is raised.

The fall effect seems to be most pronounced for, if not confined to, reactions involving collisions between solute and solvent molecules, and as far as can be judged is always negative. The conclusion is confirmed by independent collateral evidence.

At least three causes are recognized as responsible for the total effect. They are (1) the distribution of energy among a number of oscillators, (2) the electrostatic interaction of the polar molecules of solute and solvent and (3) the frequency of the rotation of a solute molecule in the solvent atmosphere.

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