effect of the ideas of Bohr, Kramers and Slater, which retain the principle of conservation of energy only as a statistical requirement. This would permit activation by radiation without any immediate destruction of radiant energy, and indeed might permit us to postpone the necessity of "balancing the energy account" until after the deactivation of the products of the reaction.

7. In conclusion it can be stated that activation may occur to some extent by all the four mechanisms suggested. Indeed, since the great difficulty is to account for the rapidity with which energy of activation is supplied, we must not despise the assistance afforded by any method of activation. However, it seems at the present as if our main hopes must be centered on the elaborated radiation theory if we are to account for unimolecular reactions, and on this theory in general if we desire to have the same mechanism of activation for all typical chemical reactions.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL AND INORGANIC CHEMISTRY, FIRST STATE UNIVERSITY OF MOSCOW]

THE VOLUMETRIC METHOD OF MEASUREMENT OF THE MUTUAL SOLUBILITY OF LIQUIDS. THE MUTUAL SOLUBILITY OF THE SYSTEMS ETHYL ETHER-WATER AND ISO-AMYL ALCOHOL-WATER

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The first part of this investigation was completed in January, 1922, and was presented at a meeting of the Chemical Club of the Laboratory of Physical and Inorganic Chemistry of the First State University of Moscow on May 15, 1922, but remained unpublished. In this first part, in which A. P. Gubkina assisted, was fully discussed the present volumetric method, the measurements being made upon two pairs of liquids: ethyl ether-water and *iso*-amyl alcohol-water. Later, Hill[1] applied the volumetric method to the determination of the mutual solubility of ether and water. The second part of the present investigation was then finished. The method used by the authors was suggested to them by Prof. I. A. Kablukov of the above university.

The methods previously employed for the measurement of the mutual solubilities of liquids are discussed at length by Hill.[1] Aignan and Dugas[2] employed a method analogous to that of the present work, but owing to a different interpretation of their results they reached somewhat different conclusions as to the applicability of this method.

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[1] Hill, THIS JOURNAL, **45**, 1557 (1923).

[2] Aignan and Dugas, *Compt. rend.*, **125**, 498 (1897); **129**, 643 (1899).

The method is based on the determination of the mutual solubility of two liquids by measurement of the quantity of each taken for mixing and the volumes of the layers at equilibrium, all measurements being made at constant temperature. Two fundamental principles underlie this procedure: (1) the law of the conservation of mass, and (2) the principle that at a given temperature the concentration of a liquid saturating a second liquid is constant, which follows from the phase rule. The experimental procedure consists in mixing known quantities of the two liquids, then measuring the volume of the two layers when equilibrium has been reached at the given temperature; the same procedure is then repeated, using other proportions of the liquids. This results in a system of equations: (I) $x_1v_1 + x_2v_2 = a_1$; $y_1v_1 + y_2v_2 = b_1$; (II) $x_1v_1' + x_2v_2' = a_2$; $y_1v_1' + y_2v_2' = b_2$, in which x_1 and y_1 are the concentrations of the liquids A and B, respectively, in the upper layer, and x_2 and y_2 are the concentrations of the respective liquids in the lower layer; a_1 and b_1 are the weights, in grams, of the respective liquids taken for the first experiment, and a_2 and b_2 the corresponding quantities in the second experiment; v_1 and v_2 are the volumes of the upper and lower layers, respectively, in the first experiment, and v_1' and v_2' the corresponding volumes in the second experiment. From these four equations the four concentrations, x_1, x_2, y_1 and y_2 can be calculated; for example, $x_2 = \dfrac{a_1v_1' - a_2v_1}{v_2v_1' - v_2'v_1}$; $y_1 = \dfrac{b_2v_2 - b_1v_2'}{v_2v_1' - v_2'v_1}$.

Aignan and Dugas[2] employed equations similar to the above but expressed all the quantities as volumes; consequently in systems where a change of volume resulted on mixing they were obliged, as in the case of ether and water, to introduce a correction for this change. When, besides this irregularity, the formation of complexes occurred, as in the case of *iso*-amyl alcohol and water, their method of calculation led to negative values of concentration. The method of calculation employed by the authors and by Hill[1] eliminates the correction for change of volume on mixing and enables the solubilities to be calculated directly from the volumetric results.

Experimental Part

Apparatus.—The measuring tube and buret used were calibrated with an accuracy of ±0.01 cc. A tenth-degree thermometer, which had been compared with a standard thermometer, was employed. The measuring tube was supported by a rubber stopper in the chamber of an ordinary refrigerator, and the thermometer passed through a second hole in the stopper. By means of long rubber tubes passing into lateral openings in the refrigerator, water at constant temperature was constantly circulated around the tube from an Ostwald thermostat, using a small water pump. The apparatus was so set up that it could be turned to any desired position, in order to stir the contents of the tube. The measuring tube had a ground-glass stopper, and no lubricant was used, in order to prevent contamination of the liquids.

Purification of Liquids.—The ether was washed five times with water, dried over calcium chloride and then distilled over sodium. The distillate was stored over sodium, and for use a quantity was removed by decantation. For each determination about 100–200 cc. was redistilled from sodium, the first fraction being rejected, and the remainder of the distillate was poured directly into the measuring tube. By this method of purification the possibility of the presence of even the smallest quantities of sodium hydroxide was eliminated, which is not assured by decantation alone. The presence of a third substance, even in insignificant amounts, may have a decided influence on the mutual solubility of two liquids, as has been shown by many investigators.[3] Therefore an energetic compound such as sodium hydroxide should be absent. It may be remarked here that the color indicators used by certain workers in this field, for example by Schuncke[4] and Klobbie[5] in the determination of y_1 in the system ether-water, may not be without influence on the mutual solubilities. The volumetric method has the advantage of requiring no color indicators. Ether purified by the above procedure boiled at 34.55° (759 mm.).

The water was distilled first with the addition of potassium permanganate, then with barium hydroxide, and the distillate was then redistilled, the middle portion being collected.

iso-Amyl alcohol was dried over anhydrous cupric sulfate, then distilled twice from calcium. The product boiled at 130.6–131.1° (760 mm.).

Procedure of Solubility Determinations.—Ether (or *iso*-amyl alcohol) was poured into the measuring tube, and a sufficient interval allowed for the liquid to subside, as determined by preliminary experiments. The volume A was then measured. Water was then added from the buret, and the liquids mixed by shaking or reversing the tube for a definite time. After complete separation into layers, the time necessary for which was also previously determined, the volumes of the layers and the temperature were recorded.

In preliminary experiments the values of x_2 and y_1 obtained by this method were compared with the corresponding values determined refractometrically, the calculations being made by means of the formula of Schütt. The measurements of n_D and d were made immediately following the volumetric measurements, so that the temperature was the same

REFRACTOMETRIC RESULTS

Temp.	$R = \frac{n-1}{d}$		$R = \frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$		Schuncke Ref. 4		Klobbie Ref. 5		Volumetric results, average (preliminary experiments)	
°C.	x_2	y_1	x_2	y_1	x_2	y_1	x_2	y_1	x_2	y_1
12°	0.060	0.008	...	...	0.083	0.019	0.084	0.008	...	...
14°	...	...	0.056	0.022	...	...	...	...	0.076	0.015

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[3] Dolgolenko, *Z. physik. Chem.*, **62**, 499 (1908). Tolloczko, *ibid.*, **20**, 389, 412 (1896). Aignan and Dugas, Ref. 2. Crismer, *Z. physik. Chem.*, **18**, 678 (1895); **24**, 551 (1897). Timmermanns, *ibid.*, **58**, 129 (1907). Schreinemakers, *ibid.*, **23**, 649 (1897).

[4] Schuncke, *Z. physik. Chem.*, **14**, 331 (1894).

[5] Klobbie, *ibid.*, **24**, 615 (1897).

in both. Loss of ether by evaporation was prevented by covering the refractometer cup with glass and by making the measurements as rapidly as possible. The results are given on the preceding page.

The difference between the volumetric and refractometric results led to an attempt to verify Schütt's formula. Unsaturated solutions of ether in water of known concentrations were measured for n_D and d, and the weights of ether taken and found were compared. In two experiments, 3.077 and 3.370 g. of ether were taken, respectively, and the corresponding weights of ether, calculated from the refractometric measurements, were found to be 2.55 and 2.64 g., respectively. This proved the inaccuracy of the Schütt formula, which is based on the assumption of the law of addition, and is therefore only approximate. Osaka[6] has called attention to the unreliability of this formula when applied to determinations of solubility. These experiments showed that the volumetric results could not be standardized against refractometric results.

In the determinations of the system ether-water at 30°, since the operating temperature is close to the boiling point of ether, with a consequent high vapor pressure in the measuring tube, some loss by volatilization of ether took place. After each series of determinations from 10° to 30°, therefore, a determination at 15° was made to measure the loss of ether, which was found to be greatest in the experiments in which ether predominated. The maximum loss was 0.01–0.05 cc., and occurred only at this temperature. No loss of *iso*-amyl alcohol was noticed in the determinations of the system *iso*-amyl alcohol-water.

Two corrections had to be applied. The first was that for loss of ether at 30°, mentioned above. The values a_1 and a_2 were those affected by this loss and were corrected. The second correction was necessary on account of the shape of the liquid meniscus. The upper meniscus was hemispherical, and the central point was easily read; but the meniscus between the two liquids was spherical and introduced the difficulty of determining the point for reading. The volume between the upper and lower levels was found to be 0.20–0.22 cc. in determinations in which the ether or *iso*-amyl alcohol predominated, and 0.26–0.28 cc. in determinations in which water predominated. The correction was made by reading the lower point in all cases and adding or subtracting from the volume so measured 0.10 or 0.14 cc. (depending on whether volatile solvent or water predominated) these corrections being one-half the total volume of the meniscus.

The System: Ether-Water

The results for the system ether-water are given in Col. 4, Tables I and II, in percentages by weight. The values found by the authors for

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[6] Osaka, "Memoirs of the College of Science and Engineering," Kyoto Imperial University, vols. I and II.

TABLE I

THE SOLUBILITY OF ETHER IN WATER

				Ether in water layer			
				Hill			
Temp. °C.	x_2	Density of water layer ($x_2 + y_2$)	K. and M. %	Calcd. %	Found %	Schuncke %	Klobbie %
10	0.088	0.9818	8.994				
		.9818	8.987				
		.9815	9.025				
		.9805	9.036				
		Av. 0.9814	Av. 9.01	9.009	9.04	8.76	9.02
15	.077	.9828	7.899				
		.9826	7.834				
		.9823	7.870				
		.9827	7.875				
		Av. 0.9826	Av. 7.87	7.89	7.913		
20	.068	.9838	6.908				
		.9835	6.832				
		.9829	6.881				
		.9836	6.879				
		Av. 0.9834	Av. 6.88	6.904	6.896	6.97	6.48
25	.059	.9840	6.075				
		.9844	6.031				
		.9842	6.033				
		.9842	6.039				
		Av. 0.9842	Av. 6.04	6.049	6.027		
30	.053	.9834	5.35				
		.9841	5.337				
		.9841	5.339				
		.9828	5.34				
		Av. 0.9836	Av. 5.34	5.327	5.34	5.99	5.04

the solubility of ether in water are seen to be close to those calculated and determined by Hill.[1] The solubilities of water in ether, given in Table II, although not agreeing with those of Hill are in general closer to his results than to those of Klobbie and those of Schuncke. The lack of agreement of determinations made at the same temperature could not be improved by repeating the experiments, and it was concluded, therefore, that in cases of low solubility, such as the solubility of water in ether, the volumetric method fails to give exact results. This is due to the error in reading the volumes of the layers in the measuring tube; in the present work the diameter of the latter was 1 cm., and the accuracy of measurement was ±0.01 cc., which is the limit of error of the results. Hill's values for the solubility of water in ether at a given temperature agree more closely, but he gives no indication of the method that he used to combine his experiments. The value y_1, and consequently the solubility of water in ether, depends chiefly on experiments in which ether predominates; similarly, x_2 is principally based on experiments in which water predominates, but as x_2 in the system ether-water is relatively large, the values for

TABLE II

THE SOLUBILITY OF WATER IN ETHER

Temp. °C.	y_1	Density of ether layer	K. and M.	Percentage of water in ether layer			
				Hill			
				Calcd.	Found	Schuncke	Klobbie
10	0.0105	0.7308	1.445				
	.0082	.7296	1.114				
	.0103	.7314	1.414				
	.0088	.7291	1.206				
		Av. 0.7302	Av. 1.30	1.164	1.164	2.63	1.09
15	.0106	.7254	1.455				
	.0088	.7252	1.21				
	.0104	.7257	1.438				
	.0093	.7238	1.279				
		Av. 0.7250	Av. 1.35	1.223	1.240		
20	.0107	.7202	1.49				
	.0096	.7199	1.342				
	.0113	.7207	1.564				
	.0100	.7189	1.39				
		Av. 0.7199	Av. 1.45	1.283	1.264	2.65	1.22
25	.0113	.7148	1.575				
	.0106	.7152	1.482				
	.0124	.7163	1.737				
	.0108	.7140	1.513				
		Av. 0.7150	Av. 1.58	1.342	1.338		
30	.0124	.7100	1.748				
	.0119	.7130	1.667				
	.0142	.7133	2.00				
	.0118	.7096	1.67				
		Av. 0.7114	Av. 1.77	1.401	1.409		1.35

it are in good agreement, as is shown in Table I. Each of the values of x_2 and y_1 is the result of combining different "direct" determinations (those in which water predominated), with different "inverted" determinations (in which ether predominated). On the other hand, better agreement can be secured by combining each "direct" determination with the corresponding "inverted" determination, as shown in Table III, in which are given the results of combining three different "direct" determinations with the same "inverted" experiment.

TABLE III

THE SOLUBILITY OF WATER IN ETHER

Temp., °C.	10	15	20	25	30
Water in ether, %	1.111	1.205	1.337	1.477	1.663
	1.124	1.212	1.342	1.482	1.667
	1.109	1.213	1.349	1.491	1.674
Av.	1.114	1.210	1.342	1.482	1.667

If the same "direct" determinations are now combined with another "inverted" determination, three new sets of values for the solubility would be obtained, agreeing well among themselves, but diverging from the values given in Table III. In Tables I and II each value for solubility is the average of four series of determinations combined as in Table III; the averages given in Tables I and II may be taken as the true solubilities.

The importance of the correlation of a and b for the accuracy of the results was noticed in preliminary experiments. This is not mentioned by Hill, but the form of measuring flask employed by him indicates that at least it was noticed, as in his work the relation a/b was always 1/3. In the present work the ratios 1/7 and 1/8 were used, giving greater accuracy. The failure of Aignan and Dugas[2] to obtain exact results was due, according to Hill, to two causes; they employed too small a volume of liquid, and introduced uncertainties in the correction for contraction. However, in the present work small volumes of liquids (40–50 cc.) were used, as in Aignan and Dugas' determinations; we concluded, therefore, that the relation of a to b is much more important than the value of either a or b. Hill used 400 cc. of liquid.

The System: Iso-amyl Alcohol-Water

The results of the solubility determinations of *iso*-amyl alcohol in water and of water in *iso*-amyl alcohol are given in Tables IV and V, respectively.

TABLE IV

THE SOLUBILITY OF *ISO*-AMYL ALCOHOL IN WATER

Temp. °C.	x_2	Density of water layer	Alcohol in water layer % by wt.	Fontein % by wt.
15	0.0306	0.9934	3.081	
	.0306	.9933	3.086	
	.0294	.9921	2.965	
		Av. 0.9929	Av. 3.04	2.72
20	.0283	.9927	2.854	
	.0284	.9935	2.857	
	.0273	.9911	2.752	
		Av. 0.9924	Av. 2.82	
25	.0268	.9921	2.703	
	.0269	.9916	2.711	
	.0258	.9906	2.610	
		Av. 0.9914	Av. 2.67	
30	.0257	.9906	2.594	
	.0257	.9909	2.599	
	.0246	.9899	2.491	
		Av. 0.9904	Av. 2.56	2.31 (29°)

The values given in the last columns of Tables IV and V are those of Fontein,[7] determined by the method of observation of the "turbidity point," in which one liquid is added to the other until turbidity occurs, the volume of the liquid added being observed and that of the second liquid

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[7] Fontein, *Z. physik. Chem.*, **73**, 212 (1910).

TABLE V

THE SOLUBILITY OF WATER IN *Iso*-AMYL ALCOHOL

Temp. °C.	y_1	Density of alcohol layer	Water in K. and M. %	Alcohol layer Fontein %
15	0.0773	0.8308	9.310	
	.0776	.8306	9.346	
	.0776	.8306	9.347	
		Av. 0.8306	Av. 9.33	9.31 (15.5°)
20	.0793	.8276	9.578	
	.0795	.8275	9.613	
	.0796	.8275	9.617	
		Av. 0.8275	Av. 9.60	
25	.0812	.8245	9.853	
	.0815	.8241	9.887	
	.0815	.8241	9.885	
		Av. 0.8242	Av. 9.87	
30	.0832	.8212	10.13	
	.0834	.8208	10.16	
	.0834	.8209	10.16	
		Av. 0.8209	Av. 10.15	10.18 (34°)

being known. It will be observed that the results of the authors agree closely with those of Fontein. Other values for the mutual solubility of *iso*-amyl alcohol and water are given by Wittstein,[8] Balbiano,[9] Verschaffelt[10] and Herz.[11]

The results in the system *iso*-amyl alcohol-water confirm the necessity, discussed above, of a proper correlation of a and b. Aignan and Dugas,[2] employing volumes of liquids of the same order as in this work, obtained absurd values of solubility, chiefly because of their irrational ratio a/b, as was proved by calculating values from their data in this system by our equations.

In order to make the volumetric method more accurate it is not only important to use a proper ratio a/b but also to make the readings of volume more exact. This may be effected by using narrower measuring tubes, or narrower constrictions at the points in the tubes where volumes are read; for example, the diameter 1 cm. used in this work might be reduced to 0.25 cm. If this resulted in hindering the stirring of the liquids, it would be necessary to abandon the volumetric method in determinations where the solubility is low. The method of Hill, employing flasks instead of tubes for measuring liquid volumes, has the disadvantage that such flasks are fragile and that stirring in them is difficult.

Summary

1. The volumetric method has been used to determine the mutual solubilities of ether and water and of *iso*-amyl alcohol and water.

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[8] Wittstein, *Jahresber.*, **1862**, p. 408.

[9] Balbiano, *Ber.*, **9**, 1437 (1876).

[10] Verschaffelt, *Z. physik. Chem.*, **15**, 437 (1894).

[11] Herz, *Ber.*, **31**, 2669 (1898).

2. The advantages of this method over others and methods of rendering the determinations more accurate, are discussed.

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[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 59]

THE CRYSTAL STRUCTURES OF CESIUM TRI-IODIDE AND CESIUM DIBROMO-IODIDE

By Richard M. Bozorth and Linus Pauling

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Introduction

About two years ago Clark and Duane[1] announced the discovery of certain peaks in a spectrometric study of the reflection of X-rays from crystals which they interpreted as due to X-rays characteristic of elements in the crystals and produced by such elements under the influence of the impinging beam, and reflected from the crystals at angles given by the relation $n\lambda = 2\,d \sin\theta$. They have since developed[2,3] a new method of crystal analysis based on this effect. The phenomena reported and the interpretations suggested are of interest from many view-points.[4] A further study by other investigators of the production and properties of these characteristic reflections seems therefore highly desirable.

One research of this character has already been published by Pauling and Dickinson.[5] The orthorhombic crystal of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, which had been investigated by Clark[3] and the results interpreted by the new method was further studied by means of spectral and Laue photographs with the aid of the theory of space-groups. This investigation led to the conclusions that the structure is not that given by Clark, and that his observed peaks were not produced by characteristic uranium L-radiation in the way designated by him. These results indicated the desirability of still further investigation.

Among the analyses reported in Ref. 2 are those of the orthorhombic crystals, cesium tri-iodide, CsI_3, and cesium dibromo-iodide, $CsIBr_2$. These crystals, are described by Groth[6] as orthorhombic bipyramidal,

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[1] Clark and Duane, *Proc. Nat. Acad. Sci.*, **9**, 126 (1923).

[2] Clark and Duane, *J. Opt. Soc.*, **7**, 455 (1923).

[3] Clark, This Journal, **46**, 372 (1924).

[4] For example, R. W. G. Wyckoff in his monograph on "The Structure of Crystals" (The Chemical Catalog Co., New York, **1924**, p. 80) makes the following statement: "As yet the properties of this 'characteristic reflection' are incompletely understood; but its very existence and the opportunity it offers of producing distinctive diffraction effects from only a part of the atoms of a crystal make it of immediate interest and probably of great future value to crystal analysis."

[5] Pauling and Dickinson, This Journal, **46**, 1615 (1924).

[6] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, vol. 1, p. 306.