measurements of Meyers and Jessup, which extend from 85.5 to 1300 cc. per gram to better than 0.1%. The constants of the Beattie–Bridgeman equation of state have been determined from these data and their values are given in Table I. The equation of state reproduces the data of the authors with an average deviation of 0.037 atmosphere, or 0.077% and the data of Meyers and Jessup to 0.012 atmosphere or 0.155%.

An equation was passed through the Meyers and Jessup data alone, which represents them to 0.004 atmosphere, or 0.043%.

The weight of a normal liter of ammonia calculated from the equation based on the authors' work is 0.7706 g. and that calculated from the data of Meyers and Jessup is 0.7715 g. The experimental value determined at the Bureau of Standards is 0.7713 g. and the average of all other careful workers is 0.7708 g.

The vapor pressures of ammonia have been determined from 30 to 132°. They agree very well with the Bureau of Standards values, which extend to 70°, and quite well with those of Keyes and Brownlee above 70°.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE EFFECT OF TEMPERATURE ON THE MOLECULAR SURFACE ENERGY OF BINARY MIXTURES. I

BY W. F. SEYER AND W. S. PECK

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The surface tension of pure liquids has been a subject of much investigation of late. The molecular surface energy has also received a good deal of attention, though this property has been largely studied from the concentration point of view and little attention has been paid to the effect of temperature on surface energy. It is true that Ramsay and Aston[1] determined the surface tensions of a few binary mixtures over considerable ranges and from the results concluded that in those cases examined the molecular weight of the mixture could be taken as the mean of the values for the two substances, but their work was limited to mixtures somewhat similar in properties. An extensive series of measurements has been carried out by Kremann and Meingast.[2] Unfortunately, the temperature interval over which they measured the surface tension was small and consequently little could be learned from their figures in regard to the effect of temperature on the molecular surface energy of binary mixtures.

An interesting series of solubility relationships is that shown by the

[1] Ramsay and Aston, *Proc. Roy. Soc. London*, **55**, 184 (1894).

[2] Kremann and Meingast, *Monatsh.*, **35**, 1323 (1914).

solubility of hydrocarbons in liquid sulfur dioxide.[3] In seeking an explanation for the extraordinary solubility of benzene in liquid sulfur dioxide (the liquids are miscible in all proportions), it became desirable to know the surface tensions of various solutions at temperatures lying between their freezing and boiling points. It is reasonable to suppose that in the case of complete miscibility in such chemically divergent liquids as those above, some sort of compound formation ought to exist in their solutions. While the freezing-point curve gave no such indication of chemical combination, yet it was thought that the existence of unstable complexes in solution might not be altogether precluded, and an examination of Eötvös constant, Ke, and its behavior with temperature in solutions of varying concentrations, might show that this was the case. As a result of the work of Jaeger[4] and others, the exact significance of this constant is much in doubt. It has been shown to be dependent upon the nature and size of the molecule. In this respect it is no different from other so-called constants which are connected with the various properties of liquids. Ramsay long ago pointed out that the problem dealing with the molecular weights of liquids in solution is a complex one. Upon mixing and forming a homogeneous phase, the following possibilities present themselves: either one or both of the liquids may become associated; if already associated before mixing, they may become more or even less associated; they may associate one with the other, thereby forming what are usually referred to as solvates. Association should in any case be accompanied by a low value of the Eötvös constant. The breaking down of these complex molecules would then be reflected by an increased value of Ke which should reach a limiting value of 2.12 when all the molecules were in their normal state. A higher value than the theoretical cannot be satisfactorily explained by merely assuming dissociation of the normal molecule, and Walden and Swinne[5] have therefore put forward the suggestion that this can readily be accounted for, if the size of the molecule be taken into consideration. In a similar manner, a high value of the constant in the case of binary mixtures can be explained by the formation of complexes. Additional support of the above explanation would be found if it could be shown that this constant decreased with temperature. It was with this object in view that the following work was done.

Experimental Procedure

The most suitable method for measuring the surface tension of liquid mixtures over an extended range of temperature is the differential capillary rise method as described by Richards, Speyers and Carver.[6]

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[3] Seyer and Hugget, Seyer and Gill, Seyer and Gallaugher, *Trans. Roy. Soc. Canada*, Nos. XVI, XVIII and XIX.

[4] Jaeger, *Z. anorg. allgem. Chem.*, **10**, 1 (1917).

[5] Walden and Swinne, *Z. physik. Chem.*, **82**, 290 (1913).

[6] Richards, Speyers and Carver, THIS JOURNAL, **46**, 1196 (1924).

This method requires a knowledge of the densities of the liquids, for calculating surface tension, but as this has to be determined in any case before the molecular surface energy can be obtained, it was not considered a serious objection. The pyrex capillary tubes used were found to have a variation in diameter of less than one part in two thousand. Two of these tubes having radii of 0.1125 and 0.0236 cm. were fused together in such a way as to present the appearance of a tuning fork (Fig. 1). The lower end of this was then sealed into a thick-walled pyrex tube, 2.5 cm. in diameter and 15 cm. in length. A second apparatus was made in the same way.

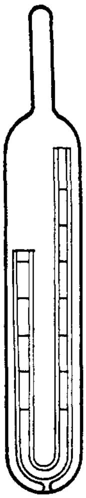

Fig. 1.

A Dewar tube served as a container for the liquids in which the surface tension tubes were to be immersed. A number of tubes were examined as regards their optical properties and the one selected as suitable was then tested further in the following manner. A surface tension tube was partly filled with water and allowed to come to room temperature. It was suspended above the Dewar tube and while in that position the difference in height of the two menisci was measured by means of a cathetometer reading to 0.05 mm. The tube was next immersed in the bath, which was also at room temperature, and the difference in height again measured through the walls of the Dewar. No difference in the two readings could be detected. Rotating the Dewar tube appeared to make no sensible difference in the cathetometer readings. Nevertheless, the tube was so marked that readings were always taken through the same region.

The next step was to determine the constant of the surface tension tubes. Richards has shown that for both tubes the following equation holds: $S = Khd$, where S is the surface tension, K a constant for the apparatus, h the corrected difference in height and d the density of the liquid minus the density of the vapor. Water was used to determine the value of the constant in the case of Tube 1 and benzene for Tube 2. These tubes were first thoroughly cleaned with aqua regia, rinsed many times with distilled water and finally water was boiled in them for some time. The tubes were then drained and again rinsed with conductivity water. After several rinsings, Tube 1 about half full of water was boiled under reduced pressure until it was thought that all air had been expelled and then sealed. After the tube had been immersed in the bath for several hours at 20°, the difference in height in the two capillary tubes was measured and found to be 4.875 cm. The correction for curvature as calculated from the known radii of the two tubes amounted to 0.0295, giving a corrected value of h equal to 4.8435. Using this and taking the value of the surface tension of water as 72.80 and the density minus the density of the vapor as 0.9982, the constant comes out to be equal to 15.026. The accuracy of this figure was then further tested by determining the surface tension of benzene at 20°. The corrected difference in height was found to be 2.1875. Taking the density of benzene minus that of the vapor as 0.8787, and inserting the above figures in the equation $S = Khd$, the surface tension of benzene is found to be 28.87. Richards, Speyers and Carver in a series of careful measurements give the value as 28.88. A second tube was then made and its constant determined in a similar manner. Its value was 18.482 and the correction for the menisci 0.0250.

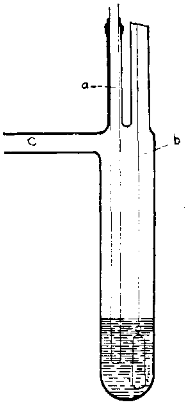

Fig. 2.

The densities were determined by three different methods. Those of the pure sulfur dioxide and of the solutions with benzene below −10° were determined by weighing a quartz bulb suspended in the liquid, which was held in a special tube (Fig. 2).

The stem of a platinum resistance thermometer (a) was placed in a limb of the tube, closed at the top with a piece of rubber. The thread for holding the sinker passed through (b). Dry air was gently blown through (c), except when actual weighings were being taken, to prevent any moisture from condensing in the bulb.

The tube itself was placed in a constant-temperature bath. The liquid inside was stirred by moving the sinker up and down. With a bulb having a volume of 8.5095 cc., the surface tension effect on the thread could be disregarded, and by always keeping the bulb the same distance below the surface, no difficulty was experienced in measuring to the fifth decimal place.

The density of pure sulfur dioxide above −15° was measured in a special form of apparatus (Fig. 3). It was essentially a dilatometer enclosed in a stout glass tube which had been carefully selected with regard to its optical properties. The chief advantages of this form of dilatometer were its compactness and the large range over which it could be used, being limited in fact, solely by the strength of the glass walls. Operation was comparatively simple. After having been evacuated, the tube was filled to one-third of its volume with liquid sulfur dioxide and sealed. Liquid could be caused to run into the inner tube by merely inverting the apparatus and cooling the upper end. When enough liquid had run in, the apparatus was righted and placed in a constant-temperature bath. As soon as equilibrium had been established, the height of the liquid in the capillary tube was read and having previously determined the volume of the bulb up to a certain mark on the capillary, and knowing the radius of the capillary (10.0282 cm.), the density of the liquid easily could be calculated.

The temperature of the bath was next raised 10° and the height of the capillary read until there was no further rise. The error introduced by the distillation of liquid from the outside tube to the inner one, owing to the difference of temperature when the bath was first warmed, was found to be extremely small and therefore negligible. The length of the capillary was sufficient to cover a range of 20°. When the liquid in the capillary stood at the top the dilatometer was placed in a bath that was 20° higher than the one in which the last measurement had been taken and enough allowed to flow out so that when the temperature was again reduced 20°, the liquid stood at the bottom of the capillary. Measurements could then be made over another 20° interval.

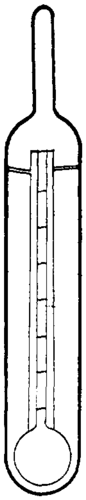

Fig. 3.

While the above method worked admirably for the pure sulfur dioxide liquid, much difficulty was encountered when attempting to measure the densities of the mixtures. This was due entirely to the wide range in boiling points comprising the mixture. The densities of these solutions were, therefore, measured in an ordinary dilatometer, sealed at the top. This, of course, introduced an error owing to the expansion of the glass, caused by the vapor pressures of the liquids. Calculation, however, showed that with the wall thickness used, no correction was necessary below 80° in the case of the different mixtures.[7]

All the usual precautions were taken to insure reasonable purity of materials used. The sulfur dioxide was obtained from Baker and Company in small iron tanks. It was bubbled through six wash bottles in series, the first one being filled with an 85% sulfuric acid solution to remove any sulfur trioxide which might be present and the remainder with concentrated acid. The gas finally passed over several feet of phosphorus pentoxide. To test its purity, the freezing point was determined very carefully in the following manner. About 20 g. of liquid sulfur dioxide was condensed in a freezing-point tube which was so constructed as to permit stirring without admission of any moisture from the air. The temperature was measured by a standardized re-

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[7] Horace Lamb, "Statics," Cambridge University Press, **1916.**

sistance thermometer with a Mueller bridge as supplied by Leeds and Northrup. After a sufficient quantity of the sulfur dioxide had been condensed, the temperature of the cooling bath was slowly lowered until crystals formed in the freezing-point tube. It was then kept constant to within one-half of a degree until all the substance was frozen. The freezing point was found to be −75.45°; this did not vary more than 0.05° while freezing was taking place. It was next allowed to melt very slowly, yielding the same figure as above for the melting point. To further test this point, sulfur dioxide was next prepared from pure sodium acid sulfite by treating it with concentrated sulfuric acid. Its melting point was −75.43 ± 0.01°. The purity of this latter material being known, the freezing point was taken as −75.43 ± 0.05°. This is considerably lower than the value given by Walden and Centnerswer, *viz.*, −72.7°. The Landolt and Börnstein tables, however, ascribe a value of −75.2°, to van der Goot. The freezing points being for all practical purposes identical, the gas from the tank was, therefore, used throughout. The benzene was the usual thiophene-free material supplied by Baker and Company and was further purified by several recrystallizations and then dried over sodium.

Proportions of Mixtures.—The wide range in boiling points of the two liquids necessitated special precautions, both in the manner of making the mixtures and in placing them in the density and surface tension tubes. Dry liquid sulfur dioxide was collected in a special glass reservoir from which it could be easily removed. To insure constancy of composition in the case of each series of measurements, it was necessary to prepare a considerable quantity of solution. This was done in the following manner. A thick-walled pyrex tube was sealed at one end and the other end sealed to a well-ground glass stopcock in such a way as to form a right angle. This container, after having been thoroughly cleaned and evacuated, was partially filled with a definite amount of benzene. Sulfur dioxide was next introduced until a solution was obtained which was approximately of the composition desired. The exact composition was then determined by weighing the tube. Distillation as a means of transferring the solution from the container to the different tube was out of the question, hence it was necessary to make sealed connections in every case and allow the solution, by inverting the container, to flow into the measuring apparatus. At the completion of each series of measurements, the composition of each solution was checked by allowing the sulfur dioxide to dissolve in alkaline solution of known strength and then titrating.

Measurement of Surface Tension.—All the temperatures were measured by a resistance thermometer which had been standardized by the U. S. Bureau of Standards and tested from time to time by determining the freezing point of water. The cathetometer could be read directly to 0.05 mm. and its accuracy was insured by focusing on a standard meter scale, standing upright beside the constant temperature bath.

Measuring the height of the liquids beolw 0° was found to be a rather difficult task. The difficulties increased with fall of temperature. Following the instructions of Richards, readings were always taken with a falling meniscus. This, however, as pointed out by Harkins and others, is apt to give too high a reading, unless sufficient time is allowed for the adhering liquid to drain back. Owing to the viscosity of sulfur dioxide at low temperatures, this required a considerable length of time. Indeed, the time required before the difference in height of the menisci became constant, when dealing with pure oxide at −50°, was between five and six hours. Irregularities in the heights and rates of fall such as are described by Bigelow and Washburn[8] when studying the variations in the surface tension of solutions were noticed. As these variations were more pronounced at low temperatures, they were at the time ascribed to the viscosities of the solutions.

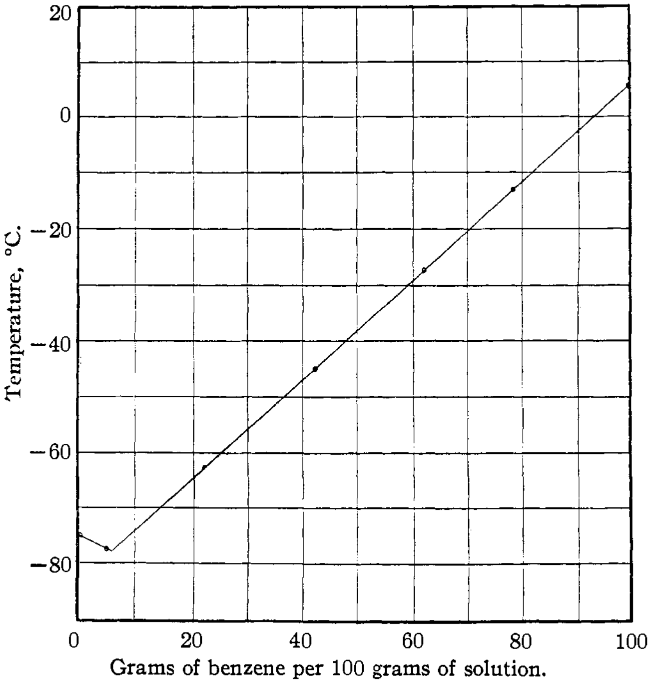

Fig. 4.—The freezing-point curve of benzene–sulfur dioxide solutions.

The densities and surface tensions of pure sulfur dioxide and of the solutions are given in the following tables. The vapor densities of the pure liquid from −50 to 0° were calculated by means of the perfect gas law and above zero by the law of Cailletet and Mathias. In calculating the vapor densities of the solutions the validity of Raoult's Law and the perfect gas law were assumed. The values of Ke were obtained by first plotting on a large scale the molecular surface energies against temperature and then calculating the constant by means of the values taken from the smoothed curve. The molecular weights in the case of the solutions were taken as

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[8] Bigelow and Washburn, *J. Phys. Chem.*, **32,** 1 (1928).

the mean of the two. Tables showing the relationships between concentrations and freezing points, and concentrations and total surface energies, are also given.

TABLE I

DENSITIES AND SURFACE TENSIONS OF PURE SULFUR DIOXIDE

Temp., °C.	Density corr. for vacuum	Density of vapor	Diff. in height corr. cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, *Ke*
−50	1.5590	0.0004	1.470	34.48	410	1.6
−40	1.5349	.0007	1.415	32.69	393	
−30	1.5106	.0012	1.365	30.91	376	
−20	1.4863	.0020	1.315	29.33	361	
−10	1.4619	.0027	1.265	27.73	344	1.8
0	1.4368	.0029	1.200	25.83	324	
10	1.4113	.0037	1.135	24.05	305	
20	1.3848	.0052	1.070	22.19	285	2.1
30	1.3574	.0073	1.000	20.30	265	
40	1.3296	.0101	1.920	18.23	241	
50	1.3007	.0140	0.850	16.43	219	2.1
60	1.2695	.0202	.785	14.73	199	
70	1.2360	.0287	.715	12.86	179	
80	1.1979	.0318	.635	11.03	155	
90	1.1568	.0479	.560	9.33	133	
100	1.1119	.0678	.485	7.60	110	

TABLE II

SOLUTION NO. 1. DENSITIES AND SURFACE TENSIONS OF SOLUTION CONTAINING 77.7% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, *Ke*
−10	0.9926	0.9917	2.136	31.83	571	2.2
0	.9799	.9787	2.051	30.16	545	
10	.9662	.9635	1.976	28.61	523	
20	.9543	.9510	1.901	27.16	502	
30	.941	.937	1.826	25.72	480	2.2
40	.929	.923	1.751	24.30	458	
50	.916	.909	1.676	22.90	437	
60	.904	.894	1.601	21.57	415	2.2
70	.892	.879	1.526	20.08	394	
80	.879	.863	1.446	18.75	371	

TABLE III

SOLUTION NO. 2. DENSITIES AND SURFACE TENSIONS OF SOLUTIONS CONTAINING 62.69% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, *Ke*
−30	1.0761	1.0758	2.090	33.79	560	2.2
−20	1.0625	1.0619	2.010	32.08	537	
−10	1.0491	1.0481	1.930	30.40	515	
0	1.0358	1.0343	1.850	28.76	489	

TABLE III (*Concluded*)

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, *Ke*
10	1.0221	1.0195	1.770	26.95	462	2.2
20	1.008	1.004	1.695	25.59	443	
30	0.994	0.989	1.620	24.09	421	
40	.980	.973	1.545	22.53	397	
50	.967	.957	1.470	21.21	377	2.1
60	.954	.940	1.390	19.73	355	
70	.938	.922	1.320	18.29	332	
80	.923	.902	1.250	16.95	311	

TABLE IV

SOLUTION NO. 3. DENSITIES AND SURFACE TENSIONS OF SOLUTIONS CONTAINING 46.01% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, *Ke*
−30	1.1191	1.1186	1.620	33.50	530	2.5
−20	1.1044	1.1035	1.545	31.45	502	
−10	1.0897	1.0882	1.470	29.52	476	
0	1.0741	1.0718	1.405	27.84	453	
10	1.0585	1.0549	1.335	26.04	428	2.3
20	1.047	1.042	1.270	24.42	405	
30	1.037	1.030	1.205	22.90	382	
40	1.026	1.017	1.140	21.39	360	
50	1.013	1.000	1.070	19.79	337	2.2
60	1.001	0.992	1.000	18.26	315	
70	0.985	.962	0.9355	16.84	294	
80	.977	.947	.8755	15.33	271	

TABLE V

SOLUTION NO. 4. DENSITIES AND SURFACE TENSIONS OF SOLUTIONS CONTAINING 22.07% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, *Ke*
−60	1.2969	..	1.615	38.72	537	2.1
−50	1.2812	..	1.555	36.79	515	
−40	1.2630	..	1.495	34.91	493	
−30	1.2468	..	1.440	33.19	473	2.2
−20	1.2313	1.2300	1.380	31.38	451	
−10	1.2149	1.2127	1.320	29.53	428	
0	1.1962	1.1929	1.250	27.57	404	
10	1.1784	1.1734	1.185	25.78	381	2.3
20	1.160	1.153	1.120	23.88	358	
30	1.141	1.131	1.055	22.06	335	
40	1.122	1.109	0.990	20.31	312	
50	1.103	1.085	.925	18.56	290	
60	1.083	1.060	.855	16.76	266	
70	1.062	1.030	.785	14.95	241	
80	1.040	1.000	.715	13.23	218	

TABLE VI

FREEZING POINTS OF BENZENE–SULFUR DIOXIDE SOLUTIONS

Benzene, % by wt.	0	5.5	22.0	46.0	62.6	77.7	100
F. p., °C.	−75.43	−77.4	−61.1	−41.0	−26.5	−13.6	5.4

TABLE VII

TOTAL SURFACE ENERGIES OF PURE LIQUIDS AND SOLUTIONS, ERGS PER SQ. CM. AT 0°

Benzene, % by wt.	0 (pure SO_2)	22.0	46	62.6	77.7	100
Surf. energ., ergs	74.6	76.4	77.5	78.2	69.9	67.2

Discussion of Results

The densities found for the pure sulfur dioxide are slightly higher than the mean of those given in the critical tables. The surface tensions on the other hand are somewhat lower than those found by V. M. Stowe.[9] From the results obtained sulfur dioxide appears to be associated at temperatures below 20°, which is to be expected from the polar nature of the molecule. With reference to the solutions it is seen that *Ke* is greater in all cases than is either that of benzene (2.13) or of sulfur dioxide, which on the basis of the Walden and Swinne relationship between the value of *Ke* and the size of the molecule would indicate the existence of a larger molecule in the case of the solutions than is found in either of the two pure liquids. The simplest solvate molecule conceivable, although the freezing-point curve gives no indication of such, would be one molecule of benzene combined with one of sulfur dioxide which, by applying the equation discovered by the above-mentioned authors, $Ke = 1.90 + 0.011\ (\Sigma\sqrt{n\mathrm{A}})$ where $\Sigma\sqrt{n\mathrm{A}}$ represents the sum of the square roots of the atomic weights of the elements comprising the molecule, calls for a value of *Ke* equal to 2.34. Solutions Nos. 2 and 3 apparently fulfil this condition at temperatures below 0°, the complex-molecule decomposing as the temperature rises. Solution No. 1 gives a constant value of *Ke* over the temperature measured. Its low value may be accounted for by assuming it to be the average of that of the excess benzene and that of the solvate. Solution No. 4 unfortunately shows an increasing value of *Ke*. It is difficult to find a satisfactory explanation to account for this increasing value on the basis of the above theory. Of course, at higher temperatures than 80° a decrease in the value of *Ke* might take place As this solution was composed of 77.93% of sulfur dioxide the value of 2.23 obtained at the temperatures below 0° might be due to the fact that some of the molecules of the sulfur dioxide were associated. If now the associated molecules were to break up faster than the solvate molecules as the temperature rose, a larger value of *Ke* would result. Irregular variations in the value of *Ke* are recorded by Ramsay and Aston.[1] Variations in the value of *Ke* with temperature are not limited to solutions but occur in nearly all pure liquids which are composed of com-

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[9] Stowe, THIS JOURNAL, **51**, 410 (1929).

plicated and rather unstable molecules. Thus Jaeger[4] found, to give only a few examples, that ethyl acetate has a value of *Ke* between −74 and 0° of 2.50, which gradually falls to a value of 1.30 above 15°. A few cases show increasing values of *Ke* with rising temperature, *e. g.*, diethyloxalic acid has a value of 1.8 below 0°, which rises to 3.6 at temperatures above 146°. In still other cases the value of *Ke* passes through a minimum. While inaccuracies in measurement might be the cause of small variations in the value of *Ke*, as suggested by Livingston and Morgan,[10] they can scarcely be held to account for the gradual drift in the up or down value of *Ke*. In any case it appears that liquids composed of complicated molecules behave as do binary mixtures.

A satisfactory explanation of the foregoing will likely be found in a combination of surface absorption theories and that of orientation as put forward by Hunten and Maass.[11]

Summary

1. The freezing points, densities and surface tensions of pure sulfur dioxide and of sulfur dioxide and benzene solutions have been measured.

2. It has been shown that sulfur dioxide is associated at low temperatures.

3. The freezing-point curve shows no compound formation.

4. The values of the Eötvös constant for binary mixtures have been shown to be dependent upon concentration and temperature.

VANCOUVER, B. C., CANADA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 229]

A COMPARISON METHOD FOR DETERMINING IONIZATION CONSTANTS WITH A QUINHYDRONE REFERENCE ELECTRODE

BY H. DARWIN KIRSCHMAN, BAKER WINGFIELD AND HOWARD J. LUCAS

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Introduction

Within recent years, the potentiometric method[1,2] of determining ionization constants of weak acids has begun to displace the conductivity method. One disadvantage of the latter is that it is necessary to make conductance measurements not only of solutions of the acid but also of those of a salt of the acid in order to compute Λ_0; another disadvantage arises from the fact that in order to obtain moderately accurate results very pure water must be used for the preparation of the dilute solutions.

[10] Livingston and Morgan, THIS JOURNAL, **33**, 643 (1911).

[11] Hunten and Maass, *ibid.*, **51**, 153 (1929).

[1] Britton, *J. Chem. Soc.*, **127**, 1896 (1925); Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

[2] Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 31 (1928).