A simple interpretation may be placed on Equation 3. T represents the kinetic energy driving force for diffusion; μ represents the resistance to self diffusion in the particular solvent; and the terms on the right represent the adjustments to μ necessary to provide the resistance to mutual diffusion. These adjustments involve the first power of cohesive energies between solute and solvent and the square root of solute diameter. Logically the exponents should be positive, since large solute size and strong solute-solvent interaction forces should tend to hinder diffusion. There appears to be a slight tendency for the correlation to predict high for self-diffusion and for mutual diffusion when the solute and solvent are quite similar. This coincides with the probability that $(\Delta H_v \Delta H_u)^{1/2}$ overestimates the solute-solvent attraction when molecules are dissimilar.

The correlation seems to work satisfactorily when the solute is small or polar. Data for water as solvent or solute tend to be handled adequately despite the deviation of water self diffusion from the assumed constant value of $D\mu/T$. There are still difficulties for polar solvents of high viscosity as is illustrated by the fact that the correlation predicts a diffusivity 72% lower than experimental data for the diffusion of water in glycerol (*10, 18*). Thus it seems best to limit application of the correlation to cases where the resultant $D\mu/T$ should be less than 1.5×10^{-7} cp. sq. cm./° K. sec.

NOMENCLATURE

D = diffusivity at high dilution, sq. cm./sec.
ΔH = latent heat of vaporization at normal boiling point, cal./gram mole
T = absolute temperature, ° K.
V = molal volume at normal boiling point, cu. cm./gram mole
μ = viscosity of solvent, cp.

Subscripts

u = solute
v = solvent

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Size Measurement of Collected Drops

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MEASUREMENTS of drops in the size range from 5 to 250 microns can be performed using a number of techniques. The diversity of techniques and the technique chosen for any particular measurement can partially be attributed to various drop compositions, to the variety of collection methods and to the proposed sizing and counting techniques. In this study, the scope was limited to measurement with an optical microscope, and the liquids considered were water, dibutyl phthalate, and No. 2 heating oil. Six methods of sizing drops collected on slides or in cells were investi-

In an experimental program using water, dibutyl phthalate, and No. 2 heating oil, the most convenient method for sizing drops in the 5- to 250-micron range was to measure the size of craters formed by the drops on a magnesium oxide–coated slide. Six methods of sizing drops collected on slides or in cells were investigated. The crater coefficient for water or dibutyl phthalate drops on a magnesium oxide–coated slide was 0.82. The observed flattening coefficients for drops on clean glass slides were 0.05 for dibutyl phthalate and 0.42 for No. 2 heating oil.

gated: cleaned-slide flattening-coefficient method, focal-length method, vertical-profile method, total-weight method, coated-slide method, and absolute method.

PROCEDURE

Determination of the size of collected drops is dependent upon relating the apparent or measured diameter after collection to the true spherical diameter before collection. In addition, the procedure must ensure that a representative sample is obtained, that the drops do not break up or coalesce upon collection, that reproducible results are obtained, and the size change from evaporization is minimized or compensated for in some precise way.

Of the various general types of experimental sizing procedures available (*3*), microscopic or photographic examination was chosen because of its inherent simplicity and reliability. Drops were formed by a spinning-disk atomizer, the size of drops being varied by changing the rotation speed of the disk. Details concerning the six sizing methods investigated follow.

Collection on Clean Slides. Clean glass slides, rinsed in a 0.1% solution of Aerosol O.T. and allowed to dry in a clean atmosphere, can be used as collection surfaces. The treatment with Aerosol O.T. is necessary because all cleaning methods leave some residue on the slide; in order to obtain a uniform surface and get reproducible results, a known residue is placed on the slide. A direct measurement of the apparent or flattened-drop diameter can be made microscopically if the drops do not evaporate rapidly. Alternatively, measurement can be made from a photograph of the flattened drops. This method is dependent upon knowledge of the flattening coefficient for the particular liquid on the treated glass slide. This flattening coefficient is the ratio of the true, spherical diameter of the drop before collection to the observed, flattened diameter after collection.

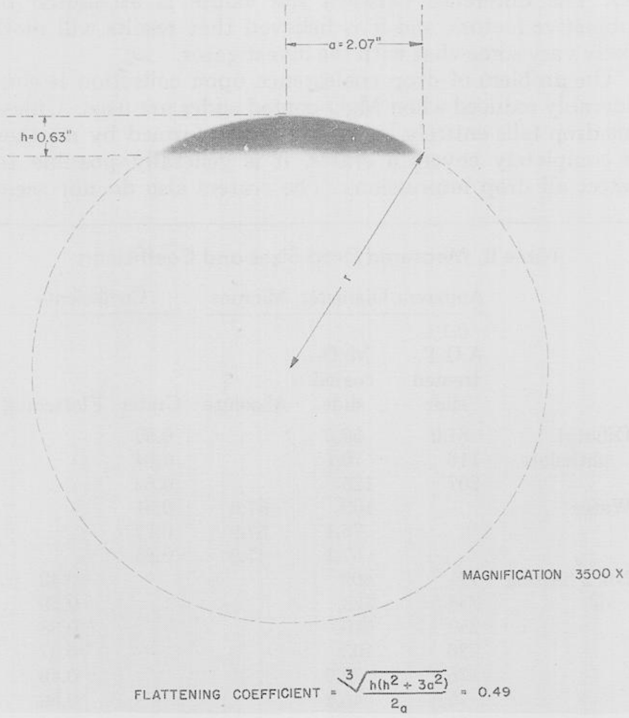

Figure 1. Profile of a flattened dibutyl phthalate droplet

Focal-Length Method. The focal-length method employs drop collection on a clean glass slide. Since the drops assume a plano-convex lens shape on the slide, a measurement of the focal length of this lens and the apparent diameter will allow calculation of the volume of the drop (*1*). The equations used to calculate drop size by the focal-length method are as follows:

Thickness

$$h = (n-1)f - [(n-1)^2 f^2 - a^2]^{1/2}$$

Volume

$$V = \frac{\pi h}{6}(h^2 + 3a^2)$$

Radius

$$R = \left(\frac{3}{4}\frac{V}{\pi}\right)^{1/3}$$

where

n = index of refraction
a = flattened radius
f = focal length
h = thickness of lens-shape drop
V = volume of drop
R = radius of spherical drop of volume V.

The flattening coefficient is given by R/a.

Vertical-Profile Method. The vertical-profile method is based upon analysis of a photograph of the drop, taken from the side. The drop is collected on a treated, clean glass slide. The vertical profile and apparent radius indicate the volume of the drop, which is assumed to attain the shape of a plano-convex lens. Figure 1 is a photograph of the vertical profile of a collected drop; the method of calculating the flattening coefficient of the drop is also shown.

Total-Weight Method. In the total-weight method, uniformly sized droplets are collected on a slide, the drops on the slide are counted, and their total weight is determined. This gives an arithmetic mass mean drop size of all the drops on the slide.

Coated-Slide Method. If a slide is coated with a layer of magnesium oxide (*2*) or soot (*5*), drops form a crater on impaction. The diameter of this crater is proportional to the true drop diameter. This true diameter can be found by means of a crater coefficient, which is the ratio of the true diameter to the crater diameter.

A photograph of the craters formed by water drops on a magnesium oxide–coated slide is presented as Figure 2. The circular portion of the light spots are the craters and the protrusions from these indicate the absorption of the water drops into the coating after collection.

Absolute Method. The absolute method gives a direct measurement of the true drop size. The drops are collected on a slide in a liquid coating layer that is slightly less dense than the drops and in which the drops are insoluble. Rupe

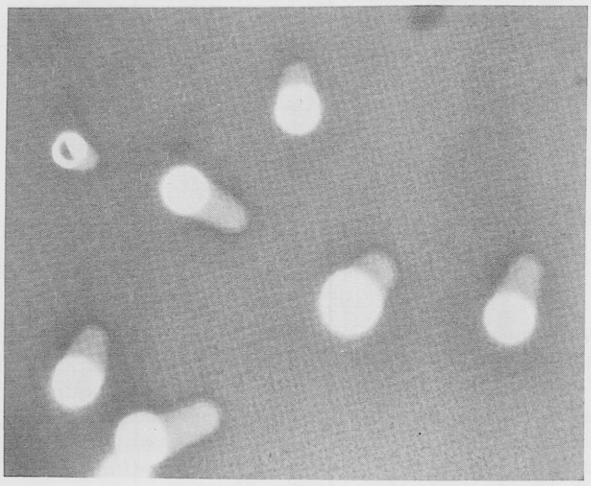

Figure 2. Craters formed by water drops on a magnesium oxide–coated slide

(*4*) outlines specifications for the collection fluid and discusses the necessary procedures.

RESULTS

The use of a spinning-disk atomizer, which forms drops that are nearly uniform in size, considerably simplifies size analysis. The degree of drop uniformity is dependent upon the liquid feed rate to the disk. The drop-size distribution is essentially a normal distribution with a very small standard deviation such as found in measurements for No. 2 heating oil with a size of 37.8 microns (flattened size is 75.5 microns). For the drops collected on a clean glass slide, the standard deviation was 1.5 microns and for those collected on a MgO-coated slide, it was 1.1 microns.

The data in Table I are measurements of individual dibutyl phthalate drops. The sizes of drops of all these liquids as presented in Table II are all the averages of about 30 individual measurements made for each entry. If these procedures are used to size polydisperse sprays, many more drops must be counted and care must be taken that a representative sample is obtained. The slower settling and impaction rates of small drops should not cause them to be ignored.

Dibutyl Phthalate. Measurements of sizes of dibutyl phthalate drops were made by the focal-length, vertical-profile, and total-weight methods. These measurements were made to determine the flattening coefficient for these drops on a clean glass slide treated with 0.1% Aerosol O.T. solution. Of various concentrations of Aerosol O.T. solution tried, a 0.1% solution gave the most consistent results. The slides were rinsed in the Aerosol O.T. and allowed to dry. The results of these measurements are presented in Table I which shows that, measured by the vertical-profile and focal-length methods, the mean flattening coefficients for dibutyl phthalate are, respectively, 0.492 and 0.497. The total-weight method gave a value of 0.50, the measurement being based on the weight of 59 drops. The crater coefficient was determined from samples collected simultaneously on a clean glass slide and on an MgO-coated slide. Since the flattening coefficient was known from previous measurements, the crater coefficient could be calculated. These results are presented in Table II. The crater coefficient was 0.82.

Table I. Flattening Coefficients for Dibutyl Phthalate Drops

Vertical-Profile Method		Focal-Length Method	
Flattened Size	Flattening Coefficient	Flattened Size	Flattening Coefficient
60.75	0.490	16.4	0.499
56.7	0.483	56.6	0.505
52.1	0.505	73.3	0.483
38.3	0.482	104.2	0.505
36.65	0.483	121.5	0.490
30.0	0.495	58.0	0.499
28.3	0.505	67.7	0.496
87.5	0.495	154.0	0.495
19.0	0.505	152.5	0.507
8.2	0.499	166.2	0.503
41.5	0.462	191.0	0.501
33.4	0.503	194.0	0.500
8.64	0.498	259.0	0.494
6.84	0.499	267.0	0.498
		273.0	0.498
	Mean =0.492	279.0	0.492
			Mean = 0.497

By total-weight method, flattening coefficient = 0.50.

Water. The size measurements for water were made by the absolute method and the MgO-coated slide method to determine the crater coefficient. The absolute method employed kerosine as the collection fluid and silicone stopcock grease as the slide coating. Results, as presented in Table II, show that the average value for the crater coefficient is 0.81.

No. 2 Heating Oil. Simultaneous samples of No. 2 heating oil were taken on a clean glass slide and on an MgO-coated slide. The results for these measurements are presented in Table II. Since the crater coefficient for the drops was independent of the liquid, a crater coefficient of 0.82, which was found for dibutyl phthalate and water, was assumed for No. 2 heating oil. With this assumption the flattening coefficient was 0.43.

Discussion. The procedure for using the absolute method proved quite difficult in that it required a considerable degree of manipulative skill. The focal-length and vertical-profile methods were also quite difficult and involved. The use of flattening coefficients is limited to liquids with low vapor pressures at working temperatures. The most convenient method seems to be the use of MgO-coated slides as collection surfaces.

May has found that the crater coefficient is independent of drop composition (*2*). This was verified for dibutyl phthalate and water as shown in Table II. The crater coefficients for impacted drops of these two liquids had essentially the same value, 0.82, which differs from May's value of 0.86 (*2*). The difference between the values is attributed to subjective factors, and it is believed that results will most likely vary somewhat with the investigator.

The problem of drop coalescence upon collection is considerably reduced when MgO-coated slides are used. Unless one drop falls entirely inside the crater formed by another or completely covers a crater, it is generally possible to detect all drop impressions. The craters also do not seem

Table II. Measured Drop Sizes and Coefficients

	Apparent Diameter, Microns			Coefficients	
	0.1% A.O.T.-treated slide	MgO-coated slide	Absolute	Crater	Flattening
Dibutyl phthalate	81.0	50.5		0.80	
	118	70.1		0.84	
	207	125		0.82	
Water		109	87.0	0.81	
		76.1	57.9	0.77	
		57.1	47.9	0.85	
No. 2 heating oil	791	409			0.42
	258	123			0.39
	250	118			0.38
	226	103			0.37
	126	72.0			0.46
	75.5	46.2			0.50
	71.4	38.5			0.44

to be changed by overlap and, in about one-half of the cases in which overlap occurs, size measurements are possible.

An attempt was made to determine how dependent the flattening coefficient is upon drop size for No. 2 heating oil. However, no definite trends were found. If the crater coefficient varies slightly with drop size, as is reported by May, this could obscure any noticeable effect of drop size on the flattening coefficient.

CONCLUSIONS

The flattening coefficient for drops collected on glass slides treated with 0.1% Aerosol O.T. solution is dependent upon the drop composition. This flattening coefficient may be determined by other measurement procedures. The crater coefficients for water and dibutyl phthalate drops collected on MgO-coated slides are essentially the same and equal to approximately 0.82. This agrees with the results of previous studies in two ways: magnitude of the coefficient and lack of its dependence upon drop liquid. The use of MgO-coated slides for measuring drop sizes is simple, convenient, and accurate.

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Aqueous Systems at High Temperature. XV.

Solubility and Hydrolytic Instability of Magnesium Sulfate in Sulfuric Acid–Water and Deuterosulfuric Acid–Deuterium Oxide Solutions, 200° to 350° C.

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The solubility of $MgSO_4 \cdot H_2O$ has been determined in H_2SO_4–H_2O solutions in the presence of vapor at temperatures from 200° to 350° C. and at concentrations of H_2SO_4 to 1.8 molal. Analogous solubilities of $MgSO_4 \cdot D_2O$ have been determined in D_2SO_4–D_2O over the same temperature and concentration range. In contact with solution concentrations of SO_3 (total sulfate) below approximately 10^{-2} molal at 270° to 350° C. and 0.1 molal at 200° C., the monohydrate solid (in excess) was found to be hydrolytically unstable, and converted partially either to an oxysulfate or $Mg(OH)_2$ depending upon temperature and solution concentration. Solutions of stoichiometric $MgSO_4$ in H_2O over the entire region of concentration (0.003 to 2 molal) precipitated either one or two of the solids, $MgSO_4 \cdot H_2O$ (not alone), oxysulfate, or $Mg(OH)_2$, to attain equilibrium.

IN A PREVIOUS determination of $NiSO_4$ monohydrate solubilities in H_2SO_4-H_2O and D_2SO_4-D_2O solutions at temperatures between 200° and 350° C., it was shown that $NiSO_4 \cdot H_2O$ solid, in dilute acidic solutions, converted hydrolytically to one or more nickel-oxysulfates, or to $Ni(OH)_2$ (*6*). Since Benrath (*3*) showed that near 200° C. the apparent solubility of a $MgSO_4$ solid decreased to very low values (but that an "aufscheidungskurve" existed above the true solubility curve), it was of interest to determine the phase relationships of $MgSO_4$ in H_2SO_4-H_2O solutions between 200° and 350° C. (in the presence of vapor), and to determine whether $MgSO_4$ was similar to $NiSO_4$ in its solubility and hydrolytic characteristics. The results of this study are of particular interest to distillation processes for desalination of sea or brackish water as $Mg(OH)_2$ is one of the constituents of scale that can form on heat exchanger surfaces at high temperature. Solubility measurements were made also in D_2SO_4-D_2O solution for comparison with the previously determined, analogous solubilities of $NiSO_4 \cdot D_2O$, $Li_2SO_4 \cdot D_2O$, and Li_2SO_4 (*6, 7*).

Previous solubility studies of $MgSO_4$ hydrates in H_2SO_4-H_2O solutions have been confined to temperatures between 0° and 55° C. These studies for the most part were concerned with the transition temperatures between the various hydrates as a function of H_2SO_4 concentration (*1-5, 8*). Many investigators have reported on the solubility of $MgSO_4$ hydrates in H_2O from −4.0° to 240° C. References to most of this work are given and evaluated by Seidell in his compilation of solubilities (*9*). Benrath's values are included in Seidell and Linke's supplement (*10*).

The present paper gives the solubilities of $MgSO_4 \cdot H_2O$ and $MgSO_4 \cdot D_2O$ in solutions of H_2SO_4-H_2O and D_2SO_4-D_2O, respectively, at concentrations of acid between 10^{-2} and 2 molal and at temperatures from 200° to 350° C. In addition, the hydrolytic instability at high temperature of stoichiometric $MgSO_4$ in H_2O solution, and of $MgSO_4 \cdot H_2O$