A design method is now available whereby the k_G obtained from Equation (1) can be combined with effective interfacial areas a reported previously (*10, 11, 12*) to obtain a k_Ga for any desired gas-liquid-solute system for which physical properties are available.

ACKNOWLEDGMENT

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NOTATION

A = total surface area of packing, sq. ft.
a = effective interfacial area, sq. ft./cu. ft.
D_v = diffusivity of solute in gas, sq. ft./hr.
D_P = diameter of sphere possessing the same surface area as a piece of packing, ft.
G = superficial gas rate, lb./(hr.)(sq. ft.)
H.T.U. = height of a gas-phase transfer unit, ft., $(G/k_GaM_MP_{BM})$
j_D = mass transfer factor, defined by Equation (1)
K_G = over-all mass transfer coefficient, lb. moles/(hr.) (sq. ft.)(atm.)
k_G = gas-phase mass transfer coefficient, lb. moles/(hr.) (sq. ft.) (atm.)
k_L = liquid-phase mass transfer coefficient, lb. moles/(hr.)(sq. ft.) (lb. moles/cu. ft.)
M_M = mean molecular weight of gas, lb./lb. mole
N_A = rate of mass transfer, lb. moles/hr.
p = partial pressure of naphthalene in the gas, atm.
$(\Delta p)_{lm}$ = logarithmic mean driving force, atm.
P_{BM} = mean partial pressure of inert gas in the gas phase, atm.
T = absolute temperature, °K.
t = temperature of the gas, °C.
u = gas velocity, ft./sec.

Greek Letters

ϵ = void fraction, cu. ft./cu. ft.
μ = gas viscosity, lb./(hr.)(ft.)
ρ = gas density, lb./cu. ft.

Subscripts

S = at the naphthalene surface
S_1 = at the naphthalene surface, bottom of packing
S_2 = at the naphthalene surface, top of packing
1 = bottom of packing
2 = top of packing

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Densities of Liquid-acetone-water Solutions up to Their Normal Boiling Points

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The densities of acetone-water liquid solutions have been measured over the entire composition range from 20°C. to within 3° to 7°C. of the normal boiling point of the mixture. The density was measured with a Robertson pycnometer (*13*), which was modified slightly. The density values are thought to be accurate to within ±0.00005 density units. The technique for determining density values of the volatile mixture near the boiling temperature is given in some detail. The refractive index (n_D^{25}) of pure acetone has been redetermined and equals 1.35596 ± 0.00003.

In a study of the effect of the physical properties on the efficiency of distillation in the binary acetone-water system, physical properties such as density, viscosity, molecular diffusivity, and surface tension were needed at the boiling temperature. No density data of acetone-water mixtures above 25°C. could be found in the literature; furthermore, no reliable method was known whereby the density data could be extrapolated 30° to 75°C. to the boiling points with confidence. It was resolved to measure the density precisely (at least to ±0.01%) from 20°C. to within a few degrees of the boiling temperature. These data could then be used to extrapolate accurately to the boiling points. Measurements and correlations of other physical properties such as the absolute viscosity, the surface tension, and molecular diffusivity require accurate density values, and the density data would also be useful in this respect.

Several early investigators (*8, 10*) have reported the densities of acetone-water mixtures at 15°, 20°, and 25°C. Their results, however, scatter considerably, probably because of the inferior quality of the acetone available to them. The most recent, and presumably the best, determinations of the densities of acetone-water mixtures were done by Young (*16*) at 20°C. and by Griffiths (*5*) at 25°C.

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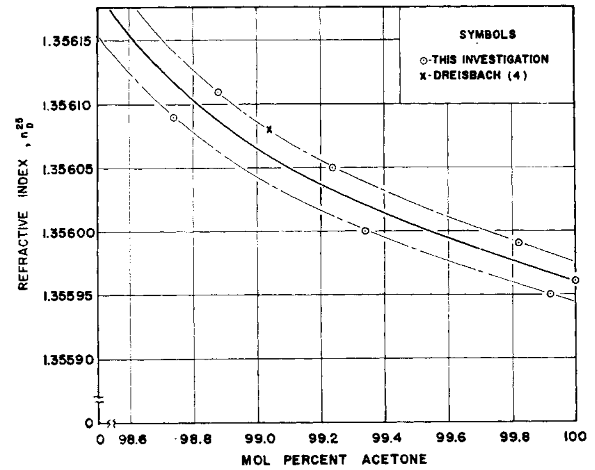

Fig. 1. Refractive index of acetone-water solutions, high acetone concentration.

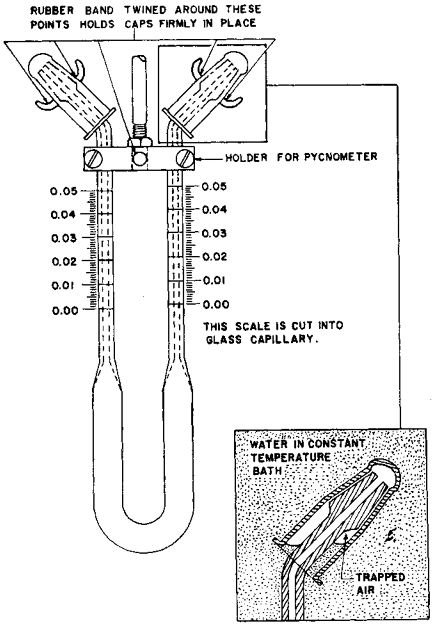

Fig. 2. Modified Robertson pycnometer.

Table 1. Density of "Pure" Acetone at 20.00°C.

Density, g./ml.	Reference
0.792	*7*
0.79082	*15*
0.79079 (99.70 wt. %)	*4*
0.79061	*16*
0.79060	*15*
0.79053	*15*
0.78990	*14*
0.7895	*2*
0.7894	*12*
0.7894	*6*

The density of pure water is, of course, known very accurately, but not the density of pure acetone. Density values for "pure" acetone at 20.00°C. are listed in Table 1. The agreement of density values of acetone at other temperatures is no better (*15*). Thirion and Craven (*14*) made a careful study of the density and dryness of acetone and concluded that the most accurate density of pure acetone at 20.00°C. was 0.78990 g./ml. Small amounts of water increase the density, while isopropyl ether, a probable contaminant if the acetone is manufactured from isopropanol, will reduce the density. Careful measurements of the density of acetone-water mixtures in the range of 0 to 5 wt. % of water were made by Young (*16*) at 20°C. The acetone that Young used as pure, however, had been dried over calcium chloride for one week and had a density of 0.79061, an indication that it was not yet completely anhydrous. Tests in the authors' laboratory show that the water content of acetone continues to decrease even after 6 months with calcium sulfate as the desiccant. Using Thirion's (*14*) 100.00% density value of 0.78990 g./ml. and drawing a curve parallel to Young's in the region of 0 to 5 wt. % water in acetone is an accurate means of predicting the water content of acetone samples from precision density measurements. This was the primary standard by which the water content of the acetone used in this work was determined. Dreisbach's (*4*) density value for 99.70 wt. % acetone (99.04 mole %) is 0.79079. The value read from the aforementioned curve at 99.04 mole % is 0.79078, showing excellent agreement with this method. The secondary standard was the refractive-index vs. water-composition curve. A record was made of the refractive indexes of the acetone samples the water contents of which had been determined by density measurements. These data are given in Table 2 and Figure 1.

Table 2. Refractive Indexes and Densities of Concentrated Acetone-water Solutions

Mole % acetone	Density at 20°C., g./ml.	Refractive index, n_D^{25}
99.92	0.78998	1.35595
99.82	0.79007	1.35599
98.74	0.79106	1.35609
98.88	0.79093	1.35611
99.24	0.79061	1.35605
99.34	0.79059	1.35600
100.00	0.78990	1.35596*

*This value was extrapolated from the data of Figure 1.

The dashed curves in the figure are approximately ±0.00002 refractive index units from the solid, median curve. The instrument with which the measurements was made is accurate to ±0.00003 unit. It is seen from the figure that Dreisbach's (*4*) point at 99.04 mole % acetone is well within the rated accuracy. From this graph the water content of the "pure" acetone was checked each time an acetone-water mixture was made up. In this way the mole percentages of acetone reported are thought to be accurate to within ±0.1% of the value of the composition.

EXPERIMENTAL PROCEDURE

A 10-ml. Robertson pycnometer (*13*), obtained from the Scientific Glass Apparatus Company of Bloomfield, New Jersey, was modified as shown in Figure 2. The modification consisted of putting a skirt on the caps which would allow the entire pycnometer, including the caps, to be immersed in the constant-temperature bath without the ground glass of the tips being wetted. When the bath temperature was above room temperature, it was necessary to immerse the entire pycnometer to prevent condensation of the acetone-water mixture in the caps.

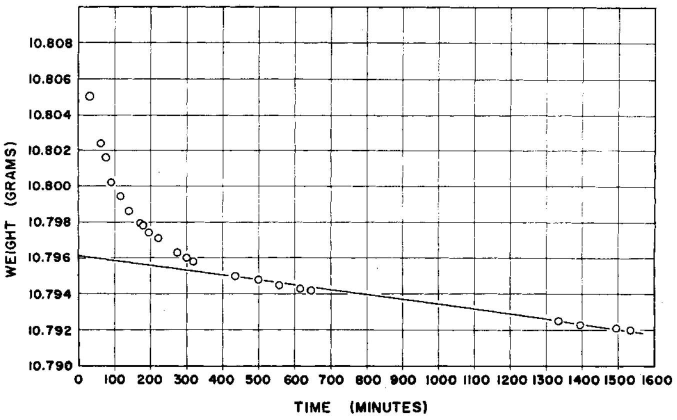

Fig. 4. Pycnometer weight as a function of time.

Bauer's (*1*) technique for precision pycnometric measurements was followed carefully except for a few modifications which became necessary. The standard liquid used for calibrating the pycnometer was tap water that had been distilled once in a Barnstead still and redistilled in an all-quartz apparatus (*9*).

The acetone used in this investigation was Baker Analyzed Reagent Grade, Baker and Adamson Reagent Grade, and Fisher Certified Reagent, Spectroanalyzed. Thirion and Craven's (*14*) test for isopropyl ether indicated that this impurity was not present. The three acetone sources were also analyzed in a Fisher-Gulf Partitioner (a gas chromatography unit) and the results showed that water was the only contaminant, a finding that was supported by distillation studies in a laboratory still (1- by 90-cm. reflux section packed with 1/8-in. Pyrex helixes) The boiling point range was 56.1° to 56.2°C. (749 to 750 mm. Hg). The water content of the acetone was determined from density and refractive-index measurements as described.

All weights used in the calibration, in the density determinations, and in making up the mixtures were corrected to the vacuum weight. The brass weights used were compared with National Bureau of Standards calibrated weights and the corrections noted. The constant-temperature bath controlled the temperature to ±0.01°C. and the thermometer used was calibrated by the National Bureau of Standards.

The method of filling the pycnometer is shown in Figure 3. Using the ball joint as shown in the figure avoided air locks in the filling and flushing of the pycnometer. Especially at the higher temperatures it was found convenient to fill the pycnometer completely and immediately after filling to immerse it partially in an auxiliary bath 3° to 10° above the temperature at which the density was to be measured. The liquid which was forced out of the pycnometer was wiped off quickly with a dry chamois, and the caps were set in place. Enough liquid had overflowed from the pycnometer so that when it was put in the main constant-temperature bath at the test temperature, the liquid contracted and the menisci fell into the graduated range of the capillary arms. From the completion of filling until the pycnometer was placed in the main constant-temperature bath was a matter of less than 1 min. Evaporation in handling the pycnometer was negligible. Some evaporation from the liquid necessarily took place in the constant-temperature bath. The vapors filled the upper arms of the capillaries and the small volumes of the caps. It was estimated that this amount of evaporation changed the mole percentage of the liquid in the pycnometer less than 0.002 unit. The density differences resulting from this were completely unimportant to the accuracy of the measurements.

After the volume had been read in the constant-temperature bath, the pycnometer was removed and carefully wiped dry and clean on the outside with a chamois. The caps were removed, the portion of the arm under the cap skirt was quickly wiped, and clean dry caps were inserted immediately. At 37.78°C. and higher the pycnometer was removed from the bath and straightway carried to a refrigerator, where the wiping and replacement of the caps took place. In

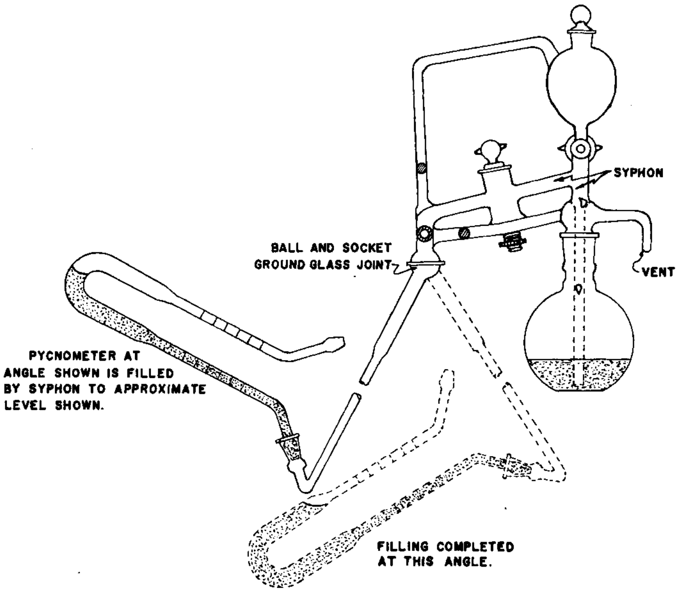

Fig. 3. Pycnometer filling procedure and apparatus.

TABLE 3. DENSITY OF LIQUID-ACETONE-WATER SOLUTIONS

Temperature, °C.	Mole % acetone	Density, g./ml.
20.00	100.00	0.78990*
	99.92	0.78998
	99.82	0.79007
	99.34	0.79050
	99.24	0.79061
	98.88	0.79093
	98.74	0.79106
	78.84	0.81344
	49.06	0.85953
	25.10	0.91613
	14.50	0.94833
	0.00	0.99823
25.00	99.58	0.78482
	80.31	0.80626
	48.21	0.85617
	38.02	0.87836
	25.30	0.91103
	14.55	0.94446
	6.935	0.97033
37.78 (100.00°F.)	99.58	0.77015
	76.46	0.79646
	50.12	0.83921
	37.22	0.86742
	25.02	0.90015
	14.52	0.93483
	7.166	0.96247
50.05	99.58	0.75556
	78.13	0.78003
	48.55	0.82888
	24.86	0.88911
	14.40	0.92542
	7.152	0.95486
60.11	11.00	0.93104
70.20	4.716	0.95218
	2.063	0.96482
80.35	2.109	0.95971

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*Reference *14*.

this way vaporization losses were held to a minimum. The pycnometer was suspended in the left arm of the balance, a tare (dummy pycnometer) being in the right arm, and the weighings were begun. Weight-vs.-time curves, such as shown in Figure 4, were prepared. Zero time corresponded to the time of reading the volume just before the pycnometer was removed from the constant-temperature bath. The first portion of the curve represented the time period when water evaporation and water-vapor adsorption on the outside of the pycnometers were coming to their equilibrium values. At the same time some weight was being lost owing to evaporation of the liquid in the pycnometer. The former effects no longer changed the apparent weight after about 300 min., but the latter effects continued as long as weighings were made. The straight-line portion of Figure 4 represented that time period when only evaporation caused a weight change. Extrapolation of this line to zero time represented the accurate apparent weight at the time of reading the volume. The continued loss in weight must indicate the fugitive nature of acetone-water vapors in spite of tightly placed ground-glass caps. In the water-calibration runs the weight-vs.-time curve soon fell to a constant weight.

TABLE 4. DENSITIES OF LIQUID-ACETONE-WATER SOLUTIONS AT THE NORMAL BOILING POINTS

Mole % acetone	Boiling temperature*, °C.	Density, g./ml.
0	100.00	0.9584
2	86.50	0.9551
5	75.00	0.9472
7.5	70.20	0.9385
10	66.72	0.9298
20	62.17	0.8949
30	61.01	0.8623
40	60.40	0.8368
50	59.84	0.8155
60	59.30	0.7983
70	58.81	0.7823
80	58.20	0.7678
90	57.43	0.7560
100	56.20	0.7476

*Averaged values from References *2*, *3*, and *11*.

RESULTS

The results of the density measurements are given in Table 3 and Figure 5. The isotherms are shaped in a smooth curve and display a small inflection near 15 mole %. Density values read at fixed compositions from enlarged plots of Figure 5 were cross-plotted as functions of temperature from which the densities at the boiling temperature were obtained by extrapolation. The values are listed in Table 4 and shown in Figure 6. Boiling-point temperatures as functions of composition in the liquid phase were determined from the average values from several sources (*2*, *3*, *11*). More weight was given to the boiling-point data of Brunjes (*2*), as they seemed to have more internal consistency. The boiling-point temperatures are probably no more accurate than ±0.1°C. The extrapolated density values therefore lack precision. Should more accurate boiling-point temperatures become available, corresponding density values can be extrapolated with a precision to match that of the measured density values.

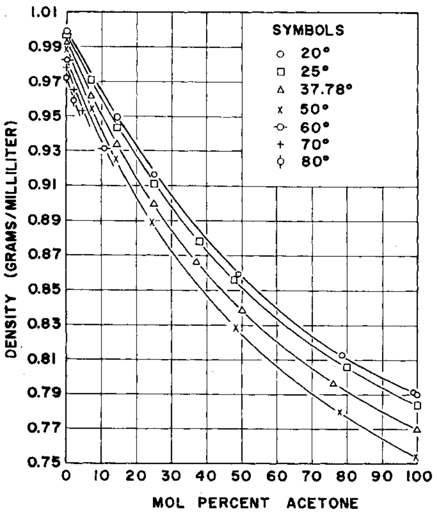

Fig. 5. Density of liquid-acetone-water solutions.

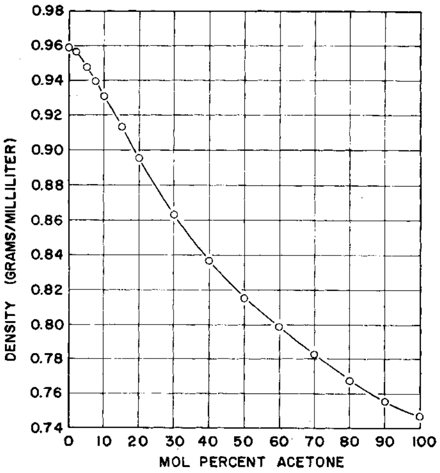

Fig. 6. Densities of liquid-acetone-water solutions at the normal boiling points.

DISCUSSION

The pycnometer was calibrated at 20°, 25°, and 60°C. Two runs were made at each temperature, one run with water at a low level in the calibrated arms of the pycnometer and another at a high level. If the milliliters per scale division in each arm were assumed to be equal at the given temperature, the volume of the pycnometer with both menisci at the zero scale reading was a straight-line function of temperature and was expressed as an equation derived by the method of least squares.

Calculation of the difference of the calibration points from the least-squares calibration curve gave the average expected error in the volume readings as ±0.000175 ml. With ±0.0002 g. allowed as the maximum error in the vacuum weights calculated along with the volume deviation mentioned above, the error in the density measurements was estimated as ±0.00003 density unit. The figure given in the abstract for the accuracy of the density values of ±0.00005 is a conservative one.

The accuracy of the reported mole percentage is discussed above and estimated as ±0.1% of the reported composition.

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