then that selectivity of removal could be effected by choosing a collector that has coordination or chelation properties selective for the component to be removed. Ionic strength also affects the degree of separation by ion flotation by directly altering the ionic competition for the collector as it is being carried to the foam phase. Selectivity then could be improved in some systems by adjusting the concentration of neutral salts as well as the pH.

Precipitate Flotation Systems. Iron and copper hydroxide precipitates were removed from dispersion using several types of collectors. As with ion flotation, coordination effects were observed; stearylamine, for example, efficiently removed copper hydroxide but not iron hydroxide. The removals of iron by the nitrogen collector were non-reproducible and reached a limiting removal of about 82%. It is concluded that the lack of reproducibility of the results was largely due to the variable character of iron hydroxide precipitates (19), and that a maximum removal was observed because iron and stearylamine form an unstable complex. NaLS efficiently removed both copper and iron precipitates; most likely differences in coordination were not observed because of favorable charge effects between collector and metal hydroxide.

The strong acid collector, NaLS, was more efficient for

removing iron than the weak acid collector, stearic acid. This effect occurs because of competition between metal and protons for the latter collector, lauryl sulfate maintaining its negative charge even in very acid solutions. In general, removals with NaLS were rapid and virtually complete within a relatively short period of time.

The experimental data for iron(III) agreed very well with the calculated precipitate formation curve demonstrating the applicability of hydrolysis data for predicting and comparing removals by precipitate flotation. Because of differences in precipitation points among transition metals, it is very likely that separations can be effected by simple pH adjustment. The separation of metals by this technique should be examined in more detail.

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Some Aspects of Thermoelectric Vapor Pressure Osmometry

Arnold Adicoff and Warren J. Murbach

Organic Chemistry Branch, Code 5056, Research Department, U.S. Naval Ordnance Test Station, China Lake, Calif. 93555

The thermoelectric vapor pressure osmometer has been established as a satisfactory instrument for the determination of the vapor pressure lowering of solutes in solutions. The calibration constant, a_1 , of the instrument is demonstrated to be independent of the nature of the solute and can be calculated from a knowledge of the system geometry and measurable thermodynamic and transport parameters. Experimental results have been evaluated in terms of the change in resistance of the thermistor and the concentration of solution. It was necessary to use a second degree equation in concentration plot to fit the data. Evaluation of the coefficient of the second order term has required the incorporation of a heat of mixing term in the form of the Van Laar equation. The concentration independent term β for the heat of mixing was obtained for 14 solutesolvent pairs.

WITHIN THE LAST FEW YEARS, interest in a rapid and precise method for measuring the number-average molecular weight of low molecular weight polymers and prepolymers has increased. In the range of molecular weights of polymers below 10,000 the thermoelectric technique has become popular. Ebullioscopic and cryoscopic methods require difficult differential techniques for the highest sensitivity and suffer markedly from problems that lead to such complications as limited solvent choice, foaming, coprecipitation, solvation, and molecular stability. These methods are often tedious and time consuming. The thermoelectric method on the other hand is rapid, requires small samples, and permits a wide choice of solvents. In addition, recently, the method is said to have been extended to polymers of 40,000 molecular weight (1). It therefore became of interest to determine the extent to which a popular commercially available instrument for thermo, electric determinations could be used as a research tool, andif possible, determine the necessary conditions for its proper use as such a tool.

A number of authors (1-14) have utilized the method of Hill (15) to measure either vapor pressure differences or, from these differences, molecular weights of solutes. A paper by Tomlinson and coworkers (12) has reviewed vapor phase osmometry and calculated thermodynamic efficiencies for a number of solvent systems and Van Dam (13) has optimized a thermoelectric vapor phase osmotic system using thermocouples and a detailed analysis of the mass and heat transport

- (2) E. J. Baldes, Biodynamica, 46, 1 (1939).
- (3) E. J. Baldes and A. F. Johnson, Ibid., 47, 1 (1939).
- (4) A. P. Brady, H. Huff, and J. W. McBain, J. Phys. Colloid Chem., 55, 304 (1951).
- (5) D. E. Burge, J. Phys. Chem., 67, 2590 (1963).
- (6) W. I. Higuchi, M. A. Schwartz, E. G. Rippie, and T. Higuchi, J. Phys. Chem., 63, 996 (1959).
- (7) S. Kume and H. Kobayashi, Makromol. Chem., 79, 1 (1964).
- (8) R. H. Müller and H. J. Stolten, ANAL. CHEM., 25, 1103 (1953).
- (9) J. J. Neumayer, Anal. Chim. Acta, 20, 519 (1959).
- (10) R. Pasternak, P. Brady, and H. Ehrmantraut, Paper presented at the ACHEMA 1961, 13th Chemical Engineering Congress, June 1961, Frankfurt am Main, Germany.
- (11) G. B. Taylor and M. B. Hall, ANAL. CHEM., 23, 947 (1951).
- (12) C. Tomlinson, Ch. Chylewski, and W. Simon, *Tetrahedron*, **19**, 949 (1963).
- (13) J. Van Dam, Rec. Trav. Chim., 83, 129 (1964).
- (14) A. Wilson, L. Bini, and R. Hofstader, ANAL. CHEM., 33, 135 (1961).
- (15) A. V. Hill, Proc. Roy. Soc. (London), A127, 9 (1930).

M. J. R. Cantow, R. S. Porter, and J. F. Johnson, J. Polymer Sci., A2, 2547 (1964).

Table I. Properties of Toluene-2,4-dicarbamates



^b Literature m.p. 83° C (17).

R

• Previously prepared by Henry (18), m.p. 117-118° C; F, 46.32%.

to measure molecular weights up to 14,000. Van Dam has estimated the upper limit of this method to be 30,000 with an accuracy of 10%.

Calculations of molecular weight using the vapor osmometer are based upon a calibration of the instrument with a purified, low molecular weight solute of known molecular weight. This constant is often called the instrument constant and has been calculated by Tomlinson (12) from the dimensions of the instrument, the thermal balance factors such as solvent evaporation from the cell, thermal conduction, solute diffusion through the drop, and diffusion of solvent through the cell atmosphere. This cell constant is designated as d by Tomlinson and K by Burge (5). For the sake of compatibility with the terminology of Mechrolab (16) and that used in the balance of this paper, the cell constant is defined as a_1 .

From a consideration of the work of Brady, Huff, and McBain (4), conducting the differentiation with respect to X_2 , the mole fraction of component 2, instead of vgm, utilizing Raoult's law, and followed by a rearrangement of terms, one can derive Equation 1.

$$\Delta r_2 = \frac{B_2 R M_1 r_{2,0}}{\Delta H_v \rho_1 10^3} \cdot C \tag{1}$$

i.e.,
$$\Delta r_2 = a_1 C$$
 where $a_1 = \frac{B_2 R M_1 r_{2,0}}{\Delta H_v \rho_1 10^3}$

For consistency in this paper the subscript 2 refers to the solute system and the Brady *et al* r_1 's and r_2 's have been interchanged for the purposes of this paper. The notation $r_{2,0}$ refers to the resistance of the sample thermistor conditioned to pure solvent at $T = T_0$, the cell temperature. Further approximations used in deriving Equation 1 involve the assumption that $X_2 \cong n_2/n_1$ and that the density of the solution ρ_s can be approximated by the density of the solvent ρ_1 . B_2 is the semiconductor constant of the sample thermistor in degrees Kelvin, Δr_2 is the change in the resistance of the sample

thermistor in ohms, R is the gas constant in kilocalories per mole per degree, ΔH_v is the heat of vaporization of the solvent in kilocalories per mole, T is the absolute temperature in degrees Kelvin, and M_1 is the molecular weight of the solvent. It is also further assumed that the heat of vaporization of the solvent from the solution can be closely approximated by the heat of vaporization of the pure solvent.

Ν

7.45

4.80

3.52

It was of interest, therefore, to establish the degree to which a_1 is a constant for a number of solutes of differing molecular weights. It was also of interest to explore to some degree the significance and mode of plotting data customarily obtained during a molecular weight determination. In order to achieve this end, a number of pure model compounds were used covering a range of molecular weights from 135 to 1238. To obtain compounds in the higher molecular weight range. use was made of the reaction of a diisocyanate with good samples of the available fluorinated alcohols.

EXPERIMENTAL

Solutes. Acetanilide (National Bureau of Standards Microanalytical Standard 141) was used as received.

1,3-Dinitrobenzene (Eastman Kodak Co.) was recrystallized five times from ethanol-water (2:1); m.p. 91.3-91.5° C.

Benzil (Fisher Scientific Co.) was recrystallized twice from absolute ethanol; m.p. 95.3-96.0° C.

2,4,6-Tribromoaniline (Eastman Kodak Co.) was recrystallized three times from 95% ethanol; m.p. 121.0° C.

Toluene-2,4-dicarbamates. The dicarbamates were prepared by direct reaction of toluene-2,4-diisocyanate (TDI) and the appropriate alcohol. The synthesis of bis(1,1,7trihydroperfluoroheptyl) toluene-2,4-dicarbamate illustrates the general procedure. Pure 1,1,7-trihydroperfluoro-1-heptanol (36.5 grams, 0.11 mole), freshly distilled TDI (8.7 grams, 0.05 mole), and a few crystals of ferric acetylacetonate were mixed in a 125-ml Erlenmeyer flask protected with a drying tube. After the exothermic reaction had subsided the mixture was heated on a steam bath for 1 hr. After cooling, the resultant crystalline mass was crushed under 50 ml of carbon tetrachloride, collected, and washed with two 50-ml portions of carbon tetrachloride. The product was then repeatedly recrystallized from the appropriate solvent to a constant melting point.

The data for the dicarbamates are presented in Table I.

Solvents. Toluene (reagent grade), acetone (electronic grade), and 1,2-dichloroethane (technical grade) were all

⁽¹⁶⁾ Mechrolab, Inc., VPO Technical Bulletin No. 11.

⁽¹⁷⁾ R. G. Bossert, J. Org. Chem., 23, 906 (1958).

⁽¹⁸⁾ R. A. Henry, U. S. Naval Ordnance Test Station, China Lake, Calif., private communication, 1966.

Table II. Resistance–Temperature Characteristics of VPO Thermistors at 37° C

Thermistor	Resistance, ohms	Temperature coefficient, ohm/ohm/° C	Semiconductor constant B, ° K
Reference	6064	-0.0416	4004
Sample	6016	-0.0419	4030

obtained from Baker and Adamson Products and were used without further purification.

1,2-Dimethoxyethane (Eastman Kodak Co.) was dried over CaH₂ and LiAlH₄ and then distilled from fresh LiAlH₄ through an Oldershaw column. A middle fraction was collected; b.p. 81.7° C/710 mm.

Instrumentation. All measurements were made at 37° C with a vapor pressure osmometer (Model 301A) manufactured by Mechrolab, Inc., Mountain View, Calif. The variation of the resistance of the thermistors with temperature was measured over the range 36.00 to 38.00° C and the temperatures were recorded to the nearest one-thousandth of a degree and the resistance measured to the nearest one-tenth ohm. Thirty data points for each thermistor showed no deviation from the straight line plot of $\log_{10} r vs. 1/T$. Müller and Stolten (8) also verified the linearity of this plot over the range 23.572 to 25.726° C. The matching of the thermistors used in these experiments is listed in Table II.

When measurements were attempted with a volatile solvent such as acetone, solvent was lost from the sample syringe because of capillary attraction between the ground surfaces of the plunger and barrel. This resulted in a slow increase in the observed Δr value when replicate measurements were made on a sample solution. To overcome this difficulty, the instrument was equipped with gas-tight syringes having a Teflon-tipped plunger fabricated by the Hamilton Co., Whittier, Calif. These syringes have the same general dimensions as those supplied with the instrument and, therefore, no modification of the syringe holder was required. By using the new syringes, sample solutions could be left in the thermal block for several hours without a detectable drift in the Δr value.

Measurement Technique. Solutions used in measurements of Δr were prepared immediately before use by direct weighing of the solute into a 25-ml volumetric flask. Measurements were carried out under as nearly identical conditions as possible. Syringes were placed in the thermal block and allowed to come to temperature for at least 15 minutes. The technique employed in zeroing and balancing the instrument was essentially the same as that suggested by the manufacturer. Subsequently, a drop of the test solution was placed on the sample thermistor and readings of Δr were taken at intervals up to 6 or 8 minutes to establish an optimum reading time. At least four readings were taken at each concentration of the test solution.

In the concentration range used here this method has given consistent results. At higher concentrations, the method of extrapolation of data to zero time has apparently improved results obtained by other workers (I). The caution that should be observed in this type of extrapolation is that the extrapolation be made according to the equation derived from the proper consideration of the various heat transfer and molecular transport equations.

Calibration runs were made at concentrations up to about 0.04 mole/liter in acetone and in 1,2-dichloroethane and to about 0.07 mole/liter in toluene and in 1,2-dimethoxyethane.

Calculations. The calculations were done on an IBM 7094 Digital Computer using a program written in Fortran IV language. The program was arranged to yield the least-

Table III. Values of Coefficients in Equation $\Delta r = a_1 C + a_2 C^2$ at 37° C

	(Readin	ig time: 3 min)		
Solute	Formula weight	<i>a</i> ₁ , ohm-liter-mole	<i>a</i> ₂ , ohm-liter ² /mole ²	$s_y _x,^a$ ohm
		Acetone		
Acetanilide	135.16	450	- 352	0.04
1.3-Dinitrobenzene	168.11	449	- 357	0.03
Benzil	210.22	455	- 377	0.04
2.4.6-Tribromoaniline	329.85	453	-416	0.01
Di-n-hexyl toluene-2.4-dicarbamate	378.50	456	-457	0.04
Bis(1 1-dihydroperfluorobutyl)				
toluene-2 4-dicarbamate	574.28	458	- 368	0.03
Bis(1.1.7-trihydroperfluoroheptyl)				
toluene-2 4-dicarbamate	838.36	452	75.9	0.02
Bis(1 1 11-tribydroperfluoroundecyl)				
toluene-2 4-dicarbamate	1,238,44	455	-482	0.02
	-,	Av. 454		
	1.2-Dr	CULODOFTHANE		
	1,2-D1	CHLOROETHANE		
Benzil	210.22	349	-657	0.08
	1,2-Dim	IETHOXYETHANE		
Benzil	210.22	431 ^b	- 392	0.12
		Toluene		
Asstanilida	135 16	299	-914	0.02
Acetaninde Deseil	210 22	302	-118	0.02
2.4.6 Tribromooniling	320.85	302	- 155	0.04
2,4,0-1 fibroinoainine Dis(1,1,7 tribudroporfluorobentul)	529.85	502	100	0.04
toluone 2.4 dicarbamate	838 36	299	-911	0.03
ionicite=2,4-uicarbamate	656.50		~	0.05
		Av. 301		

^a Standard error of estimate.

^b Reading time: 6 min.

squares best estimates of the virial coefficients of the equation

$$\Delta r = a_0 + a_1 C + a_2 C^2 + a_3 C^3 \tag{2}$$

as well as the calculated values of the dependent variable $(\Delta r')$, the vertical deviations of the observed points from the sample regression line $(\Delta r - \Delta r')$, and the standard error of estimate $(s_{y,x})$.

When $a_0, a_2, a_3 = 0$, Equation 2 reduces to Equation 1.

RESULTS AND DISCUSSION

A careful examination of the representative calibration data for the four solvent systems, i.e., toluene, 1,2-dichloroethane, 1,2-dimethoxyethane, and acetone seen in the representative curve for acetone (Figure 1) reveals a curvature requiring a consideration that $a_{0}, a_{2}, a_{3} \neq 0$. Table III presents the data for the case that $a_{0}, a_{3} = 0$. This form of Equation 2 can be written as either Equation 3a or Equation 3b as used by Billmeyer and Kokle (19)

$$\Delta r = a_1 C + a_2 C^2 \tag{3a}$$

$$\frac{\Delta r}{C} = a_1 + a_2 C \tag{3b}$$

The form of Equation 3a was used to calculate the values in Table III rather than Equation 3b, because Equation 3b has, in several cases, tended to give the plotted line an upward curvature for data obtained at lower concentrations. In practice the use of Equation 3b in place of Equation 3a is justified only when a correlation factor of 1.0 exists between the errors in C and Δr . If the correlation factor is not known it is safer to use Equation 3a. The data obtained by the authors indicate that the correlation is not good.

An attempt was made to improve the fit by allowing a_0 , $a_3 \neq 0$ in the computer program. The analysis of the data indicated that no significant improvement was observed. In fact, the better fit of the data is obtained by requiring that $a_0 = 0$ (20).

Evaluation of Constants a_1 and a_2 . In attempting to evaluate a_1 and a_2 one can refer to a good thermodynamic treatment of solutions as in the chapter by Hermans in the volume of the series edited by Kruyt (21). An examination of Equation 4 reveals that the Raoult's law used in deriving Equation 1 is a special case of Equation 4

$$\frac{p}{p_0} = (1 - X_2) \exp(\Delta h_0 / RT)$$
 (4)

where Δh_0 , the heat of dilution, is zero for ideal solutions. Incorporating this term and defining Δh_0 by Equation 5

$$\Delta h_0 = \beta \overline{\nu}_2^2 \tag{5}$$

where β is the Van Laar heat of mixing and $\bar{\nu}_2$ is the volume fraction of solute, one can derive Equations 6a and 6b in a fashion similar to the derivation of Equation 1.

$$\Delta r_{2} = \frac{B_{2}Rr_{2,0}}{\Delta H_{v}} \left[\frac{M_{1}}{\rho_{1}10_{3}} C + \left(\frac{M_{1}^{2}}{2\rho_{1}^{2}10^{6}} - \frac{\beta M_{2}^{2}}{RT_{0}\rho_{2}^{2}10^{6}} \right) C^{2} \right]$$
(6a)
$$\Delta r_{2} = \frac{B_{2}Rr_{2,0}}{\Delta H_{v}} \left[\frac{M_{1}}{\rho_{1}M_{2}10^{3}} C_{w} + \right]$$

(19) F. W. Billmeyer, Jr., and V. Kokle, J. Am. Chem. Soc., 86, 3544 (1964).

(20) R. U. Bonnar, M. Dimbat, and F. H. Stross, "Number-Average Molecular Weights," p. 136, Interscience, New York, 1958.

(21) J. J. Hermans, "Colloid Science," H. R. Kruyt, ed., Vol. II, pp. 58, 64, 67, Elsevier, New York, 1949.



Figure 1. Calibration curve for bis(1,1,11-trihydroperfluoroundecyl) toluene-2,4-dicarbamate in acetone at $37^{\circ}C$

Reading time: 3 min. The filled circles represent data obtained 2 months later

$$\left(\frac{M_1^2}{2M_2^2\rho_1^2 10^6} - \frac{\beta}{RT_0\rho_2^2 10^6}\right) C_w^2 \right]$$
(6b)

where C_w is the weight concentration of solute in grams per liter. From Equation 6a the coefficients a_1 and a_2 can be defined as

$$a_{1} = \frac{B_{2}Rr_{2,0}M_{1}}{\Delta H_{v}\rho_{1}10^{3}}$$
$$a_{2} = \frac{B_{2}Rr_{2,0}}{\Delta H_{v}} \left(\frac{M_{1}^{2}}{2\rho_{1}^{2}10^{6}} - \frac{\beta M_{2}^{2}}{RT_{0}\rho_{2}^{2}10^{6}}\right)$$

From Equations 1 and 6a, the constant a_1 can be obtained in terms of measurable system constants. The thermistor constant B_2 was determined from the plot of the logarithm of the resistances vs. the reciprocal of the absolute temperature in the region of 37° C. From the evaluation of a_2 , values of β can be calculated.

Determination of Effective Heat of Vaporization. A consideration of the value to be used for the heat of vaporization in this equation must be made. The theoretical heat of vaporization gives values for a_1 that are small; the effective heat of vaporization $(\Delta H_t)_{eff}$ must, therefore, be less than the theoretical heat of vaporization. This problem has been considered in great detail in an excellent publication by Tomlinson *et al.* (12).

In this paper the treatment of Tomlinson was applied to calculate the thermodynamic efficiency, η_{rale} , from the various measured system constants. If the thermodynamic efficiency can be calculated, then the constant a_1 can be calculated. The difference in geometry and construction of the Tomlinson apparatus and that used in these experiments is sufficient to begin to evaluate the general nature of the treatment. It should be noted here that the Tomlinson thermistor was encased in a thin glass tube requiring a correction for the thermistor stem. This correction in the case of this paper is zero because no such stem was present. In addition, in this paper the thermistor leads are stainless steel rather than platinum and therefore the appropriate stainless steel con-

Table IV.	Calculated	and	Experimentally	Determined	Heat	Losses
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		Tomlir	ison (12)			
	Н	Heat loss contributions				
	Conduction		Conduction		This	work
Solvent	through gas phase c_v/ab	Radiation from drop c _r /ab	through wire <i>c_w/ab</i>	Efficiency η_{calcd}	$(a_1)_{\text{theor}^a}$ ohm-liter/mole	Efficiency η_{exp}
Acetone 1,2-Dichloroethane	0.0506	0.0178	0.0196	0.919	485 484	0.936^{b} 0.721
1,2-Dimethoxyethane	0.222	0.063	0.069	0.738	601	0.717
Toluene	0.565	0.144	0.159	0.535	579	0.520
^a Calculated from equa ^b $n_{\rm equa} = 0.93$ has been	tion in reference (4).	1 301 vapor pressur	e osmometer at 3	$39^\circ C(I)$		

Table	V.	Apparatus	Constants	Used in	Calculating	Thermo
	dvna	mic Efficier	ncies Accor	ding to	Tomlinson ()	12)

Constant	Value ^a
r_t (radius of thermistor bead)	0.055
r_d (radius of drop)	0.110
r_c (radius of cell)	2.10
r_w (radius of stainless steel wire)	0.005
l_c (length of cell)	1.00
l_w (length of stainless steel wire)	3.00
y (distance between thermistor axes)	0.40
T_0 (absolute temperature of cell)	310.0
k_w (steel)	0.111

^{*a*} T_0 is in units of °K and k_w in units of cal/cm sec deg; all other values are in cm.

ductivity was used. Further, the drop size was variable but was found to vary from about twice the diameter of the thermistor to about three times the thermistor diameter. At three times the thermistor diameter, the drop appeared almost ready to fall from the bead. Since it has already been demonstrated by a number of workers (3, 4, 11, 22, 23) and verified by the authors that the results are quite independent of the drop size in the concentration range of interest, a value for the drop diameter of twice the thermistor diameter was assumed. In the thermodynamic efficiency calculations when the drop diameter was assumed to be three times the thermistor diameter, the change in the calculated thermodynamic efficiency was very slight.

Tomlinson defines the thermodynamic efficiency η as the ratio of the measured instrument constant to the theoretical instrument constant where the theoretical instrument constant is defined to be the value obtained in the absence of any heat losses and diffusion effects. For the purposes of this paper η can be considered as $(a_1)_{exp}/(a_1)_{theor}$. The Tomlinson ΔS , the change in the shape factor caused by the proximity of the solvent and solution thermistors, was found to be very small for this system, i.e., 0.015 cm, and was neglected. The agreement between the calculated and measured thermodynamic efficiencies is quite good as can be seen in Table IV. The apparatus constants used for these calculations are presented in Table V. Attempts were made to preserve the notation of Tomlinson except where a conflict with other notation in this paper arises. Table VI presents the solvent constants. The general constants of Tomlinson were used as required. The agreement appears to be sufficiently good to state that the Tomlinson treatment of the thermal losses does

account, quite well, for the observed thermodynamic efficiencies. In these calculations, the authors have found a dearth of information concerning parameters such as thermal conductivity and diffusion coefficients for solvent vapors either pure or in the presence of air. In the case of 1,2-dimethoxyethane, a substitution of the constants of ethyl acetate was used in the place of 1,2-dimethoxyethane except where the vapor pressure and heat of vaporization at 37° C were required in which case the vapor pressure and heat of vaporization of 1,2-dimethoxyethane were used. The thermal conductivity of the solvent vapor-air mixture was calculated by Equation 7 (27c).

$$k_{s-a} = \frac{X_s k_s M_s^{1/3} + X_a k_a M_a^{1/3}}{X_s M_s^{1/3} + X_a M_a^{1/3}}$$
(7)

In this expression, the subscript s refers to solvent vapor at 37° C, the subscript *a* refers to air at 37° C, and the subscript *s*-*a* refers to the solvent vapor-air mixture at 37° C; and X is the mole fraction, k is the thermal conductivity, and M is the species molecular weight. For the purpose of these calculations k_a = 6.30 imes 10⁻⁵ cal/cm sec deg and the total pressure of the atmosphere was assumed to be 710 torr, the prevailing atmospheric pressure at the laboratory location. No transport information was found by the authors for the 1,2-dichloroethane system. Constants for a comparable or analogous system to the 1,2-dichloroethane system were not found.

Of the factors used in the calculations, the crudest were of the system geometry. Fortunately the computation can be carried out in such a fashion that the results are not very sensitive to the errors in measurement of the cell dimensions. In the equation for the thermal loss, the largest term is the loss caused by conduction through the vapor, c_v . This term contains the geometrical or shape factor and is given by Equation 8 where the terms are defined in Table IV as they are in the Tomlinson paper (12).

$$\eta = \frac{1}{1 + \frac{c_v + c_r + c_w}{ab}} \tag{8}$$

Equation 8 is a rearranged form of Equation 33 in reference (12). The consequence, therefore, is that the relative contribution of the largest contributor term is independent of the shape factor and dependent upon thermal constants. It is possible to vary the shape factor by 10% and not affect the thermodynamic efficiency by more than 0.4% when the thermodynamic efficiency is about 90%. The lower the thermodynamic efficiency, the smaller is the effect of shape

⁽²²⁾ R. R. Roepke, J. Phys. Chem., 46, 359 (1942).

⁽²³⁾ W. Simon and C. Tomlinson, Chimia, 14, 301 (1960).

Table VI. Solvent Constants at 37° C

Mol. wt. <i>M</i> , g/mole	Heat of vapor. ΔH_v , cal/mole	Density d ₄ ³⁷ , g/ml	Diff. coeff. into air D, cm ² /sec	Vapor press. p, torr	$k_s \times 10^5$, cal/cm sec deg
58.08	7479ª	0.77063	0.150°	377.7	2.91 ^d
98.97 90.12 92.13	8014° 8518' 9004 [;]	1.2287 ^b 0.8480 ^g 0.8512 ^k	0.0986^{h} 0.0974^{c}	125.7 51.5	2.74° 3.79°
	Mol. wt. <i>M</i> , g/mole 58.08 98.97 90.12 92.13	Mol. wt. M , g/moleHeat of vapor. ΔH_v , cal/mole58.087479^a98.978014^e90.128518'92.139004^i	Mol. wt. M , g/moleHeat of vapor. ΔH_v , cal/moleDensity d_4^{37} , g/ml58.087479^a0.7706^b98.978014^e1.2287^b90.128518'0.8480^a92.139004^i0.8512^k	Mol. wt. M ,Heat of vapor. ΔH_v , cal/moleDensity d_4^{37} , g/mlDiff. coeff. into air D , cm²/sec58.087479a0.7706b0.150c98.978014e1.2287b90.128518f0.8480a0.0986b92.139004j0.8512k0.0974c	Mol. wt. M ,Heat of vapor.DensityDiff. coeff. intoVapor press.g/mole ΔH_v , cal/mole d_4^{37} , g/mlair D , cm²/sec p , torr58.087479a 0.7706^b 0.150^c 377.7 98.978014e 1.2287^b 90.128518' $0.8480a$ 0.0986^b 125.792.139004i 0.8512^k $0.0974c$ 51.5

^a Calculated from data in reference (24a).

^b Reference (25).

^c Calculated from data in reference (26) using the equation $D = D_o(T/T_o)^2(p_o/p)$ where $T = 310^\circ$ K, p = 710 torr, $T_o = 273^\circ$ K, $p_o = 760$ torr, and $D_o =$ diffusion coefficient at T_o and p_o .

^d Reference (27a).

^e Reference (28).

Calculated using the Antoine vapor pressure equation, $\log_{10} p$ (torr) = 7.2643 - 1379/(230 + t). The A and B constants were estimated using Cox chart intersection points and certain selected values of the boiling point.

⁹ Reference (29).

^h Calculated from data for ethyl acetate in reference (27b) using the equation in footnote (c) where $T_o = 303^{\circ}$ K.

* Extrapolated value from data for ethyl acetate in reference (27a).

i Calculated from data in reference (24b).

* Reference (30).

¹ Reference (31).

Table VII.	Van Laar Heats	of Mixing Calculated	l from Second Virial	Coefficients

		Heat of mixing β , kcal/mole			
Solute	Density d_4^{37} , g/ml	Acetone	1,2- Dichloroethane	1,2- Dimethoxyethane	Toluene
Acetanilide	1 . 208ª	2.67			4.66
1.3-Dinitrobenzene	1.54^{b}	2.84			
Benzil	1.242°	1.24	1.76	1.20	0.37
2.4.6-Tribromoaniline	2.590°	2.41			0.80
Di-n-hexyl toluene-2,4-dicarbamate	1.098°	0.36	• • •		
Bis(1,1-dihydroperfluorobutyl)					
toluene-2,4-dicarbamate	1.714°	0.31			
Bis(1,1,7-trihydroperfluoroheptyl)					
toluene-2,4-dicarbamate	1.820°	-0.02			0.27
Bis(1,1,11-trihydroperflucroundecyl)					
toluene-2,4-dicarbamate	1.955ª	0.11			• • •
⁴ Determined by displacement of Dow (Corning 200 Fluid (d_{i}^{37})	.9535).			

^b Estimated from literature and x-ray crystallographic data.

e Determined by displacement of water containing 0.1 wt. % 3M fluorochemical surfactant FX-176.

factor error. This latter fact is in accord with the nature of the experiment because the radial distance to the solventsaturated paper wall of the cell is different than the distance to the solvent-liquid cell surface. In addition, the distance

- (24) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Vol. V, Carnegie Institute of Technology, Pittsburgh, 1954;
 (a) Table No. 206k-E, (5) Table No. 5k-E.
- (25) International Critical Tables, Vol. III, p. 28, McGraw-Hill, New York, 1928.
- (26) International Critical Tables, Vol. V, p. 62, McGraw-Hill, New York, 1929.
- (27) "Chemical Engineers' Handbook," 4th Ed., R. H. Perry, C. H. Chilton, and S. P. Kirkpatrick, eds., McGraw-Hill, New York, 1963; (a) Sec. 3, p. 206, (b) Sec. 14, p. 22, (c) Sec. 3, p. 226.
- (28) R. R. Dreisbach, "Physical Properties of Chemical Compounds—III," p. 131, American Chemical Society, Washington, D. C., 1961.
- (29) M. H. Palomaa and L. Honkanen, Ber., 70B, 2199 (1937).
- (30) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Vol. III, Table No. 5d, Carnegie Institute of Technology, Pittsburgh, 1952.
- (31) A. K. Abas-Zade, Doklady Akad. Nauk. S.S.S.R., 68, 665 (1949).

to the liquid cell surface changes as one makes successive readings. Further, the results of the calculations are rather insensitive with respect to the drop size, because only the smaller, radiant heat loss term is affected. In this term the effect should vary as the square of the drop radius but this dependence is somewhat lessened because a function of the radius also exists in the shape factor.

Determination of Van Laar Heat of Mixing β . With the confidence in the vapor pressure osmometer as a quantitative research tool established, significance can be attached to the shape of the Δr vs. C plots. During the course of the measurements it became apparent that these curves were very reproducible and showed a high degree of consistency. Plotting the data in the form of either Equation 6a or 6b accounted for the data in a satisfactory manner. In calculating the heat of mixing term, the form of Equation 5 was chosen for the sake of convenience and simplicity. It is realized that other more complex expressions may yield to better mechanistic interpretation of the heats of mixing, particularly for systems which give negative values of β . In this paper, however, it was decided not to explore this problem further. The value of the heat of vaporization used in the calculation of β was the quantity that the authors have designated as the effective heat of vaporization $[(\Delta H_v)_{eff} =$



Figure 2. Variation of the calibration constant, a_1 , with time for benzil in various solvents

 $\eta_{exp}(\Delta H_{\varepsilon})$] and is the value that is calculated from the experimental thermodynamic efficiency.

For the evaluation of the constant, β , the required solute densities were determined in wetting systems that had no effect upon the crystal. The determination of the fluorocarbon carbamate densities was extremely troublesome and the use of a small amount of a fluorochemical surfactant was found to be useful. The surfactant proved to be useful for other crystalline substances as well. The data for 14 solutesolvent systems are presented in Table VII. The negative value of β for bis(1,1,7-trihydroperfluoroheptyl)toluene-2,4dicarbamate appears to be real and was obtained in two separate series of experiments. The reason for the unique behavior of this carbamate is not known although it may be related to a unique stiffness and consequent chain configuration. Unfortunately the unavailability of the fluorocarbon alcohols and the difficulty in the higher fluorocarbon carbamates purification prevented the study of the entire series of carbamates.

Operation Notes. In the course of the measurements made with the thermoelectric vapor pressure osmometer, some consideration should be made of the reading time that should be employed. For most purposes, as long as solvent evaporation is prevented by proper syringe design and the instrument electronics are operating very well, the reading time was not critical for most solvents. The instrument as first received was sensitive to reading time; good results were obtainable by very exactly timing both the coarse adjustment time and the final reading time to within 2 seconds. In addition, long reading times (6-8 minutes) were required. A complete replacement of the electronic tubes, however, and a subsequent short tube aging time removed the sensitivity. This was true despite the fact that all the tubes were still within the design limits. Certain solvents as the halogenated ones appeared to cause a drift. This was attributed to a timedependent chemical change in the solvent. N,N-Dimethylformamide and 1,4-dioxane were two other solvents that showed tendencies to drift.

Some additional evidence as to the changes occurring in the solvent may be inferred from data obtained with a properly functioning instrument where the calibration constant a_1 is plotted as a function of time. Some solvents required very short reading times; others required relatively long reading times. The data for the variation of a_1 with reading time are seen in Figure 2. One can see that for the 1,2-dimethoxyethane 6 minutes were required before the constant varied in a slow fashion. For toluene and acetone very short reading times could be used. For 1,2-dichloroethane the changes were sufficiently rapid to enable the use of a relatively short reading time. A number of factors not under control, such as oxygen, moisture, and gas solubility may be responsible for this effect. It should, however, be noted that the ordinate is an expanded scale and within the accuracy of most calculations used in this paper the variations of the constant are not great. For very precise work such calibration curves may indeed be required.

When the instrument was used intermittently a small but disturbing amount of experimental scatter was encountered. When measurements were made when the instrument was kept operating continuously, this scatter disappeared. A careful examination of the causes of this scatter led to a consideration of the characteristics of thermistors. The observation of Müller and Stolten (8) should be underlined and provision for continuous excitation of the thermistors should be made in order to do very precise, quantitative work.

A calculation of the precision measure of the instrument reveals that for small Δr values, the thermistors used in these experiments were adequately matched with respect to their semiconductor constants and their resistances. The factor having the greatest effect upon the obtainable precision is the temperature control maintained by the instrument.

It is of interest to note the form of the pressure dependence of the coefficient of diffusion D [Table VI, footnote (c)]. From this relationship, one can anticipate that as one increases the mean free path of the vapor molecules or, alternately, as one lowers the gas pressure, an increase in the thermodynamic efficiency can be obtained. This is verified in the results of Higuchi et al. (6). It also can be anticipated that because the solvent does have a finite vapor pressure and c_v , c_r , and c_w (Table IV) also have finite values, thermodynamic efficiencies of 1.00 will not be obtained. At the present time, as indicated previously, the vapor diffusion, radiative, and conductive heat losses appear to be adequate to account for the observed phenomena. The additional corrections for solution mass and heat transport do not appear to be warranted. Further, it can be anticipated that some of the observed scatter in much of the published vapor pressure osmometer data may be attributed to fluctuations in atmospheric pressure. A variation of 25 mm in atmospheric pressure can give a 1.7% variation in the thermodynamic efficiency of toluene.

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