Table III. Rectification of 1,1,2-Trichloroethane–Perchloroethylene Mixtures

(Ultimate separations at about 200 to 1 reflux ratio)

Run No.	1,1,2-Tri chloroethane in Bottoms[a], Wt. %	n_D^{25} Overhead	1,1,2-Trichloroethane in Overhead[b], Wt. %	B. P., °C.	Notes
1	27	1.4755	71	112	Crosses Horsley's azeotrope
2	91	1.4737	77	112	
3	76	1.4747	74	112	True azeotrope overhead
4	73	1.4747	74	112	True azeotrope overhead

[a] Calculated from material balance.
[b] From refractive index–composition curve.

taken overhead alternating between 2 to 1 and about 200 to 1 reflux ratio until a constant overhead composition was obtained. Run 3 utilized a 620-ml. charge of 69 weight % of 1,2-dichloroethane which, upon removal of 69 ml. of overhead in the same manner as before, resulted in a bottoms composition of 70 weight % of 1,2-dichloroethane rectified to an overhead composition of 62%. Runs 1 and 3 bracket the azeotropic "pinch" between 59 and 62 weight % of 1,2-dichloroethane. Therefore run 4 was made with 155 ml. of 61 weight % of 1,2-dichloroethane. Removal of 88 ml. of overhead yielded overhead material of precisely the same composition as the bottoms (alternating between 2 to 1 and 200 to 1 reflux ratio). The azeotropic composition is, therefore, 61 weight % of 1,2-dichloroethane–39 weight % of trichloroethylene. This value can be considered to have the same ±1% degree of precision as the previous azeotropic composition. The corrected boiling point is 82.2° ± 0.2 °C., determined as before.

1,1,2-Trichloroethane–Perchloroethylene. The same procedure was used for this azeotrope as for the two previous ones. Four distillations were carried out (Table III). In run 1 rectification of bottoms material of 27 weight % of 1,1,2-trichloroethane to an overhead composition of 71% eliminates the possibility of an azeotrope in that range. Run 2 consisted of boiling 88 weight % of 1,1,2-trichloroethane in the same manner. The final separation values were 91 weight % of 1,1,2-trichloroethane in the bottoms and 77% overhead. Runs 1 and 2 bracket the azeotropic pinch between 71 and 77 weight % of 1,1,2-trichloroethane. Runs 3 and 4 establish the actual azeotropic composition. In Run 3 76 weight % of 1,1,2-trichloroethane mixture was rectified to an overhead composition of 74%. In run 4 a 73% mixture was rectified to 74%. The azeotropic composition is, therefore, 74 ±1 weight % of 1,1,2-trichloroethane–26 ± 1 weight % of perchloroethylene. The corrected boiling point is 112.9° ±0.2°C., determined as before.

CONCLUSIONS

The boiling points and compositions of the three binary, minimum-boiling, homogeneous azeotropes investigated are:

	Composition, Weight % First Component		Azeotropic B.P., °C.	
System	This work	Lit.	This work	Lit.
Carbon tetrachloride–1,2-dichloroethane	80 ± 1	78.4(4)	75.5 ± 0.2	75.3(4)
1,2-Dichloroethane–trichloroethylene	61 ± 1	82.0(2) 56.5(3)	82.2 ± 0.2	82.6(2) 82.1(3)
1,1,2-Trichloroethane–perchloroethylene	74 ± 1	43.0(1)	112.9 ± 0.2	112.0(1)

ACKNOWLEDGMENT

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Correlation of Vapor-Liquid Equilibrium Data for Acetone-Water System

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The system acetone-water was studied by several workers and vapor-liquid equilibrium data covering a range of isobaric and isothermal conditions are available. The present work includes all data at 760-mm. pressure and below, and isothermal data below 100 °C.

VAPOR PRESSURE DATA OF PURE COMPONENTS

Acetone. To correlate activity coefficients, the vapor pressure of acetone is required. All available data (*1,8,11, 28–31*) were collected and expressed in the form of an Antoine equation,

$$\log P = 6.962 - 1120.32/(218.38 + t) \tag{1}$$

P is in millimeters of mercury. The atmospheric boiling point determined by using Equation 1 agrees well with the value given by U.S. Industrial Chemicals (*35*). Timmermans (*33*) lists values ranging from 56.1° to 56.6°C.

Water. Vapor pressure data for water are taken from Perry (*24*).

CORRELATION OF ISOTHERMAL EQUILIBRIUM DATA

All available data (*10,13,14,16,18*) at and below 100°C. were used.

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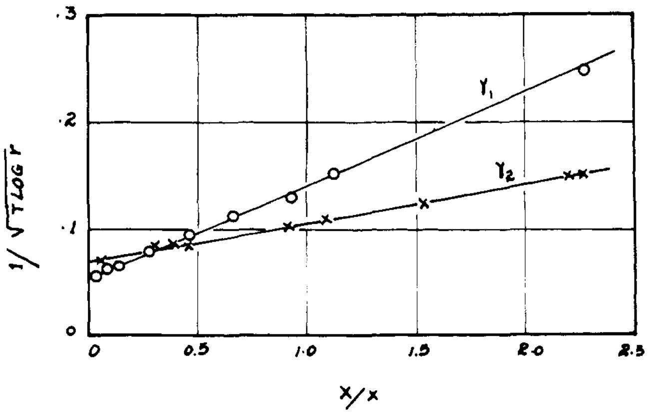

Figure 1. Li-Coull plot of activity coefficient data for 100° C.

The activity coefficients at each temperature were correlated by a form of the Van Laar equation given by Li and Coull (*15*) and White (*36*)

$$(T \log \gamma_1)^{-0.5} = m_1 x_1/x_2 + c_1 \qquad (2)$$

$$(T \log \gamma_2)^{-0.5} = m_2 x_2/x_1 + c_2 \qquad (3)$$

Figure 1 is based on the data of Griswold and Wong (*10*). The constants of Equations 2 and 3 are related to each other in the following way:

$$(m_1/m_2)^{\frac{2}{3}} = m_1/c_1 = c_2/m_2 = (c_2/c_1)^2 \qquad (4)$$

The method of Coulson and Herington (*7*) of plotting log (γ_1/γ_2) vs. x_1 is followed (Figure 2) and the area *ABC* is found to be equal to *CDE*. The data of Griswold and Wong (*10*) at 100 °C. are thus tested for thermodynamic consistency.

The basic test for consistency is the Gibbs-Duhem rule:

$$x_1(\partial \ln \gamma_1/\partial x_1)_{T,P} = x_2(\partial \ln \gamma_2/\partial x_2)_{T,P} \qquad (5)$$

Differentiating Equation 2,

$$x_1(\ln \gamma_1/\partial x_1)_T = -4.606 m_1 x_1/(T x_2^2)\left(m_1 \frac{x_1}{x_2} + c_1\right)^3 \qquad (6)$$

and

$$x_2(\partial \ln \gamma_2/\partial x_2)_T = -4.606 m_2 x_2/(T x_1^2)\left(m_2 \frac{x_2}{x_1} + c_2\right)^3 \qquad (7)$$

Substituting Equations 6 and 7 in Equation 5 and rearranging,

$$\frac{m_1}{m_2}(x_1/x_2)^3\left[\left(m_2 \frac{x_2}{x_1} + c_2\right)\Big/\left(m_1 \frac{x_1}{x_2} + c_1\right)\right]^3 = 1 \qquad (8)$$

Substituting Equations 2 and 3 in Equation 8 and rearranging,

$$\log \gamma_1 = (m_2/m_1)^{\frac{2}{3}}(x_2/x_1)^2 \log \gamma_2 \qquad (9)$$

If the data are thermodynamically consistent, a plot of log γ_1 against $(x_2/x_1)^2$ log γ_2 will give a straight line passing through the origin. This method of testing is more convenient for activity data that can be represented by Equations 2 and 3. Figure 3 shows the application of this test to some of the data: It shows that the 100 °C. data of Griswold and Wong (*10*) and 60 °C. data of Litvinov (*16*) are consistent, while the 60° and 30 °C. data of (*13*) are not consistent.

In Figure 4 values of $1/c^2$ are plotted against *T* and the best straight lines are drawn through the thermodynamically consistent points. The equations for the lines are

$$\begin{aligned} 1/c_1^2 &= 1.7821\,T - 295.32 \\ 1/c_2^2 &= 0.10442\,T + 173.711 \end{aligned} \qquad (10)$$

Values of γ_1 and γ_2 calculated from the correlating equations are compared with experimental data over the range of 25° to 100 °C. in Figure 5.

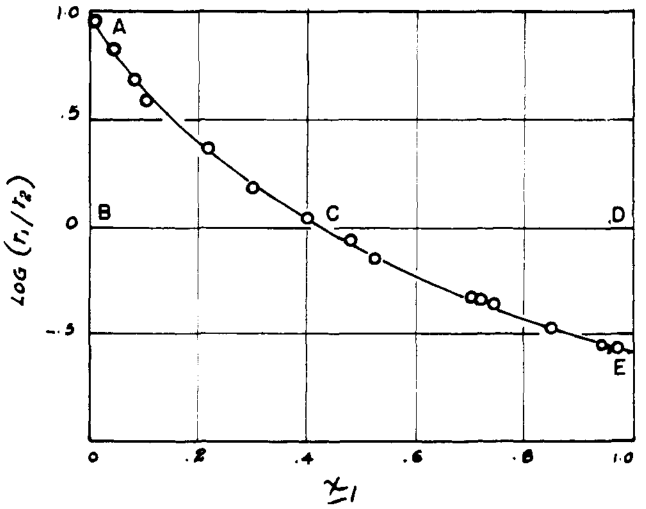

Figure 2. Test for thermodynamic consistency of activity coefficient data

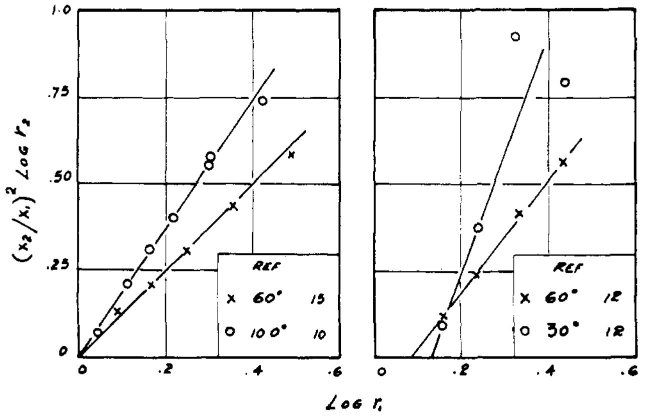

Figure 3. Test for thermodynamic consistence according to Equation 9

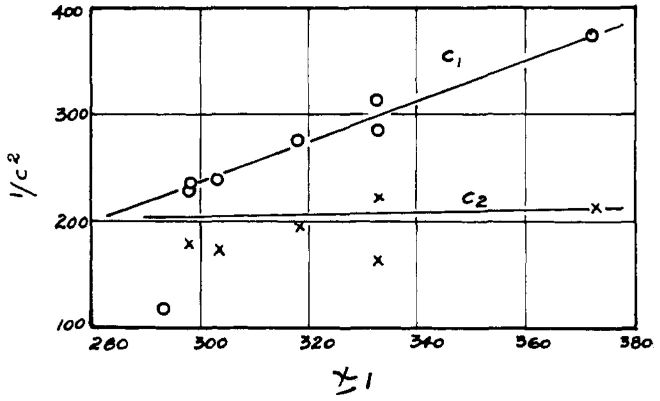

Figure 4. Correlations of constants c_1 and c_2 with temperature according to Equation 10

Table I. Vapor Pressure of Acetone

t, °C.	*P*, Mm.	*t*, °C.	*P*, Mm.
15	144.99	22.0	200
20	182.82	38.6	400
30	282.66	49.4	600
40	422.50	57.6	800
50	612.90	64.4	1000
56.14	760.00	71.5	1250
60	865.66	77.6	1500
70	1193.71	82.9	1750
80	1610.90	87.7	2000
90	2132.35	92.0	2250
100	2773.10	96.0	2500

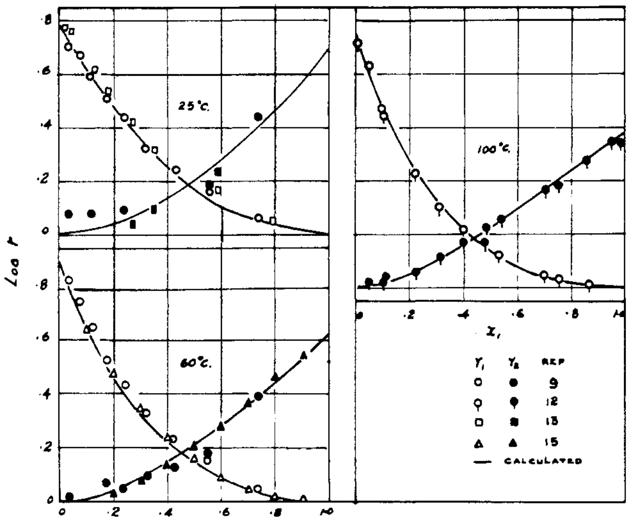

Figure 5. Comparison between calculated and observed activity coefficients for isothermal data

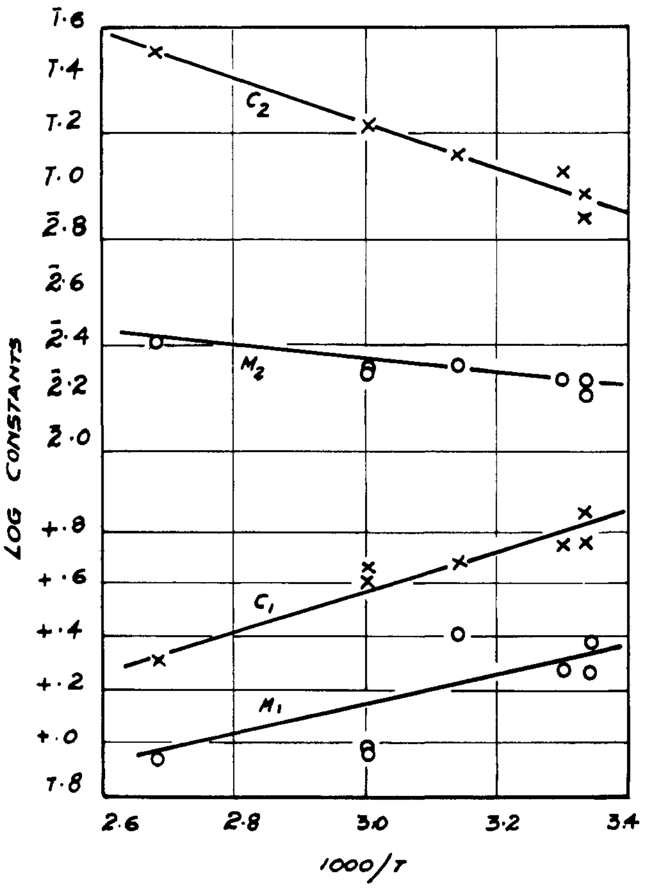

Figure 7. Correlation of isothermal Clark constants with temperature

EQUILIBRIUM DATA

Clark (*6*) and Prahl (*27*) have described methods for expressing $x - y$ data in the form of equations, which have some advantages. All the $x - y$ data can be represented by means of two linear equations, according to Clark:

$$y_1/y_2 = M_1\, x_1/x_2 + C_1 \qquad (11)$$

$$y_2/y_1 = M_2\, x_2/x_1 + C_2 \qquad (12)$$

As these two equations represent the same data, the following relation between the constants results:

$$\sqrt{M_1 M_2} \pm \sqrt{C_1 C_2} = 1 \qquad (13)$$

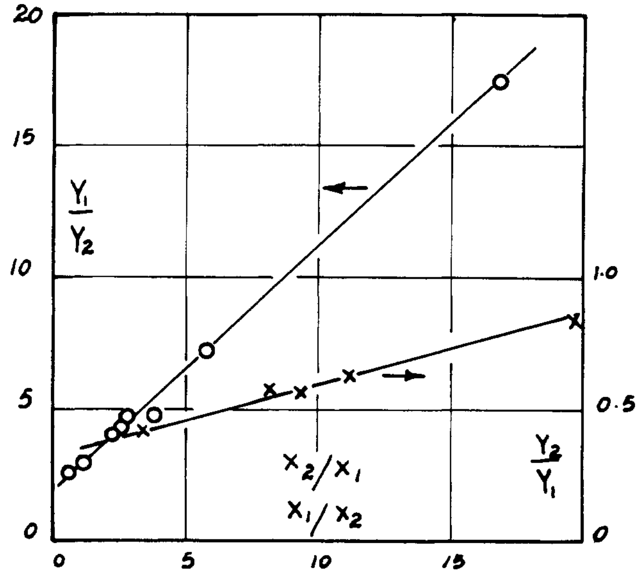

Figure 6. Clark plot of $x - y$ data for 100° C.

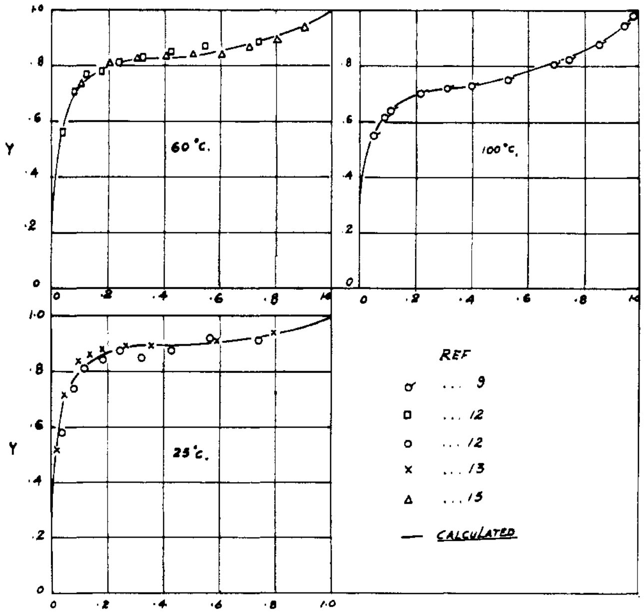

Figure 8. Comparison between calculated and observed isothermal $x - y$ data

The point which defines the limit of applicability of each equation is called the "conjugate point" and is given by

$$x_1/x_2 = \sqrt{M_2 C_1 / M_1 C_2} \qquad (14)$$

The Clark plot for Griswold and Wong's data at 100°C. is shown in Figure 6. The slope of the line for 100°C. is less than unity, indicating an azeotrope. From the correlations of constants M and C with temperature, their values at 100°C. are calculated and the composition of the azeotrope is evaluated as 98.6 mole % of acetone, using the relationship,

$$x_{1_{az}}/x_{2_{az}} = C/(1 - M)$$

The system is nonazeotropic at lower temperatures. Similar plots were made for the other thermodynamically consistent data and the constants M_1, C_1, M_2, and C_2 were calculated.

M and C are correlated with T (Figure 7) and the relations are given in Equation 15.

$$\begin{aligned}\log M_1 &= 532.82/T - 1.4416\\ \log C_1 &= 811.68/T - 1.8587\\ \log M_2 &= -259.11/T - 0.8740\\ \log C_2 &= -872.32/T + 1.8679\end{aligned}\tag{15}$$

Figure 8 compares observed isothermal data and calculated values from Equations 11, 12, and 15.

CORRELATION OF ISOBARIC DATA

Activity Coefficient Data. The isobaric activity coefficients could not be represented by straight lines according to Equations 2 and 3, as they show a marked curvature at small values of x_1/x_2 and x_2/x_1. Hence their correlation was not attempted.

Equilibrium Data, 760 Mm. A Clark plot of the $x - y$ data was first tried, but it was found that constants had to be adjusted to satisfy Equation 13; this arbitrary procedure was not favored. This is a disadvantage with all methods requiring the drawing of two lines (*4,6*). The method finally adopted was to use smoothed values from a plot of log γ_1/γ_2 vs. x, and to calculate the Clark ratios, as

$$(x_1/x_2)(\gamma_1/\gamma_2)(P_1/P_2) = y_1/y_2$$

Clark plots were prepared from these calculated ratios. The equations are:

$$\begin{aligned}y_1/y_2 &= 1.147\ x_1/x_2 + 4.600\\ y_2/y_1 &= 0.022\ x_2/x_1 + 0.153\end{aligned}\tag{16}$$

Calculated $x - y$ values are listed in Table II and compared with experimental values (*2,3,20,21,23,37*) in Figure 9.

Extensive data (*3,5,9,13,16,17,20,21,23,25,32,37*) are available for the boiling points of acetone-water mixtures at 760 mm. The data are plotted in Figure 10. The boiling points for mixtures are calculated from γ_1 and γ_2 read from a smooth curve drawn between log γ vs. x, combining with $x - y$ values calculated from Equation 16 and the vapor pressures of acetone and water. They are listed in Table II and shown in Figure 10.

Activity coefficients at 760 mm. calculated from the values of Table II are compared with experimental values in Figure 11.

Equilibrium Data at Subatmospheric Pressures. Othmer and Benenati (*20*) have made measurements at low pres-

Table II. Vapor-Liquid Equilibrium Data at 760 Mm.

t, °C.	x_1	y_1	log γ_1	log γ_2
100.00	0.00	0.0000	1.0850	0.0000
90.66	0.01	0.2975	1.0176	0.0005
84.75	0.02	0.4451	0.9624	0.0010
80.60	0.03	0.5336	0.9163	0.0015
77.50	0.04	0.5922	0.8757	0.0020
75.13	0.05	0.6340	0.8391	0.0032
70.87	0.075	0.7000	0.7622	0.0070
68.19	0.10	0.7384	0.6968	0.0100
66.32	0.125	0.7636	0.6400	0.0140
65.02	0.15	0.7813	0.5890	0.0180
63.39	0.20	0.8047	0.4998	0.0270
62.24	0.25	0.8194	0.4269	0.0435
61.45	0.30	0.8295	0.3644	0.0640
60.78	0.35	0.8369	0.3108	0.0905
60.39	0.40	0.8426	0.2615	0.1214
60.08	0.45	0.8470	0.2170	0.1492
59.91	0.50	0.8518	0.1760	0.1801
59.80	0.55	0.8571	0.1390	0.2123
59.55	0.60	0.8634	0.1080	0.2490
59.25	0.65	0.8706	0.0813	0.2896
58.79	0.70	0.8791	0.0600	0.3364
58.44	0.75	0.8893	0.0400	0.3845
58.07	0.80	0.9017	0.0235	0.4373
57.50	0.85	0.9172	0.0130	0.4992
57.07	0.90	0.9371	0.0038	0.5649
56.50	0.95	0.9634	0.0008	0.6401
54.14	1.00	1.0000	0.0000	0.7100

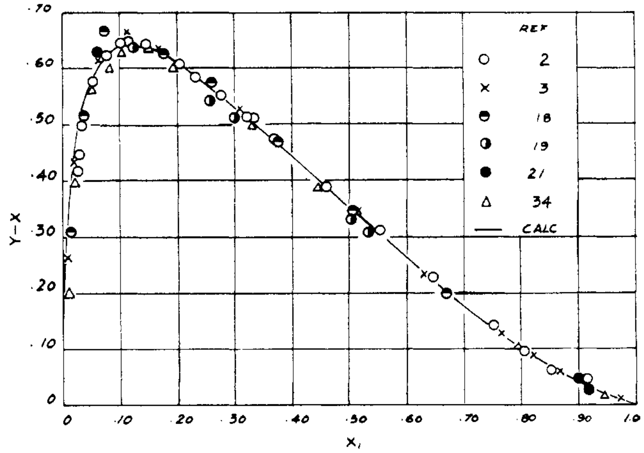

Figure 9. Comparison between calculated and observed $x - y$ data at 760 mm.

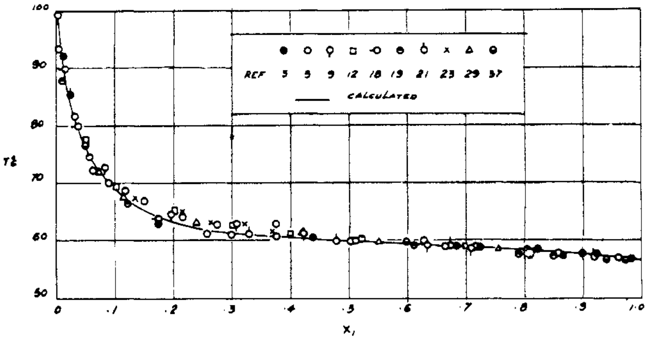

Figure 10. Comparison between calculated and observed boiling point data at 760 mm.

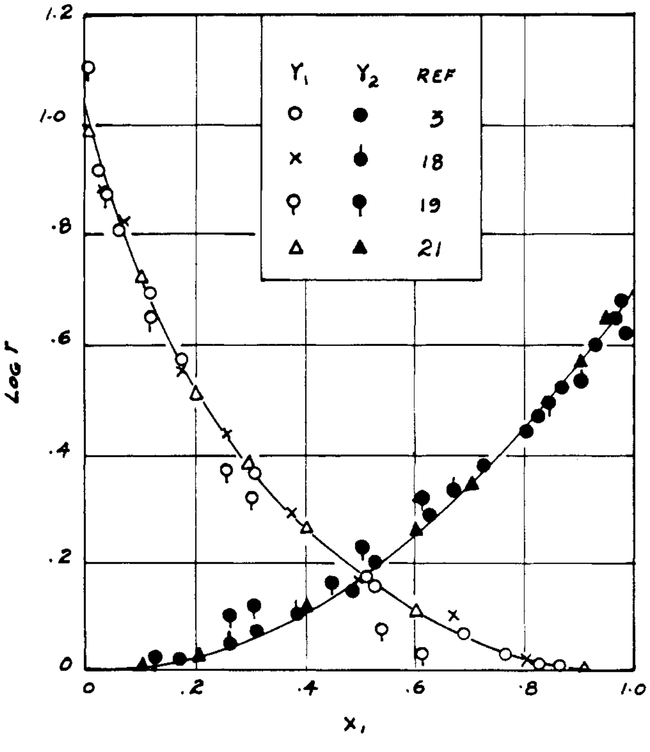

Figure 11. Comparison between calculated and observed activity coefficient data at 760 mm.

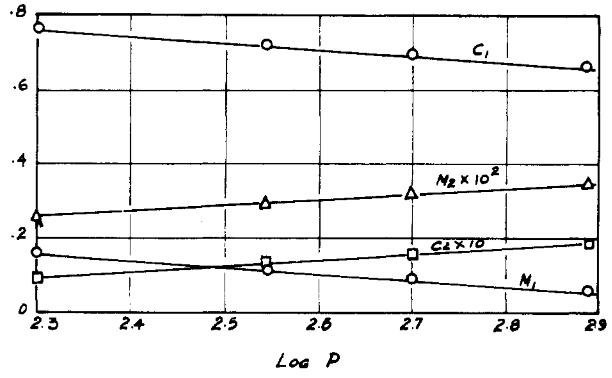

Figure 12. Correlation of isobaric Clark constants with total pressure

sures. Data are available at 500 and 200 mm. The experimental $x - y$ values at each pressure were correlated by the Clark method and the constants of the equations were obtained. The constants are plotted against pressures on log-log paper (Figure 12) and the straight lines are made to pass through the points for 760 mm. in every case. The equations of the lines are:

$$\begin{aligned} \log C_1 &= -0.16152 \log \pi + 1.1283 \\ \log M_1 &= -0.16552 \log \pi + 0.53562 \\ \log C_2 &= 0.16288 \log \pi - 1.28324 \\ \log M_2 &= 0.15972 \log \pi - 2.11212 \end{aligned} \qquad (17)$$

The constants calculated from Equation 17 satisfy Equation 13. Calculated and observed equilibrium data are compared in Figure 13.

Heat of Solution and Enthalpies of Liquid and Vapor Phases. Thermal data, such as of heats of solution and heat contents of liquid and vapor phases, are required for the design of mass and heat transfer equipment, particularly when the mixture to be handled is nonideal. As these thermodynamic quantities are related to isothermal activity coefficients, they can be easily calculated from the correlations presented in this paper; one merit of such calculated values is that they will be consistent with the $x - y$ data from which they are derived.

Heat of Solutions. The variation of activity coefficients with temperature is given by:

$$\begin{aligned} (\partial \ln \gamma_1 / \partial T) x_1 &= \bar{L}_1 / RT^2 \\ (\partial \ln \gamma_2 / \partial T) x_2 &= \bar{L}_2 / RT^2 \end{aligned} \qquad (18)$$

Othmer (22) has shown that when the logarithm γ for a particular value of x_1 is plotted against the logarithm (vapor pressure) of a reference substance at the same temperature, a linear plot is obtained.

$$\log \gamma = (\bar{L}/\lambda_r) \log P_r \text{ constant} \qquad (19)$$

Knowing the value of λ_r one can calculate $\bar{L}$ from the slope of such a plot.

Plots of the calculated values of γ_1 and γ_2 at 25°, 60°, and 100°C. against the vapor pressures of water at the same temperature (with x_1 as parameter) on log-log paper gave, in fact, straight lines, and this method was therefore used to calculate values of $\bar{L}_1$ and $\bar{L}_2$.

Table III and Figure 14 give values at 760 mm. of the total heat of solution, calculated from

$$L = x_1 \bar{L}_1 + x_2 \bar{L}_2 \qquad (20)$$

Heat Content of Liquids at 760 Mm. Boiling Temperatures. If the datum is taken as zero heat content of the pure liquids at 0°C. the heat content of liquid of composition x_1 can be calculated from

$$H_L = [cp_1 x_1 + c_{p_2}(1 - x_1)]\, t + L \qquad (21)$$

The mean specific heat, calories per gram per °C. of water, is taken as 1.0. The specific heat data for acetone, calories per gram per °C., were taken from the literature (*13,14,26,34*) and expressed in the form

$$c_{p_1} = 395/(785 - t) \qquad (22)$$

Table III. Partial and Total Heats of Boiling Solution at 760 Mm.
(Cal. per gram mole)

Mole Fraction Acetone in Liquid	$\bar{L}_1$	$\bar{L}_2$	L
0.00	1265.0	0.0	0.0
0.025	1065.0	2.7	29.25
0.05	887.5	10.3	54.15
0.10	563.0	36.8	89.4
0.15	305.0	73.5	108.2
0.20	118.2	115.0	115.6
0.30	−134.8	195.3	96.3
0.40	−236.5	248.0	54.2
0.50	−246.0	254.0	4.0
0.60	−202.0	200.0	−41.2
0.70	−135.3	20.7	−79.5
0.80	−68.5	−131.0	−81.0
0.85	−45.0	−262.5	−77.2
0.90	−18.8	−415.0	−58.4
0.95	−4.9	−586.0	−34.0
1.00	0.0	−782.0	0.0

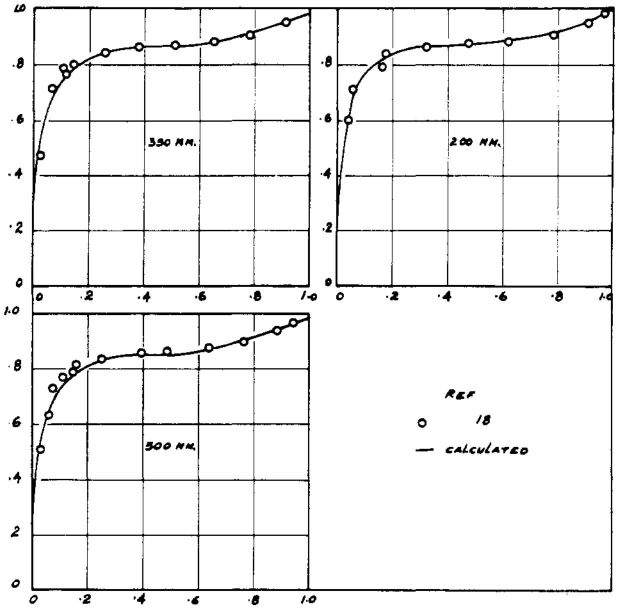

Figure 13. Comparison between calculated and observed $x - y$ data at subatmospheric pressure

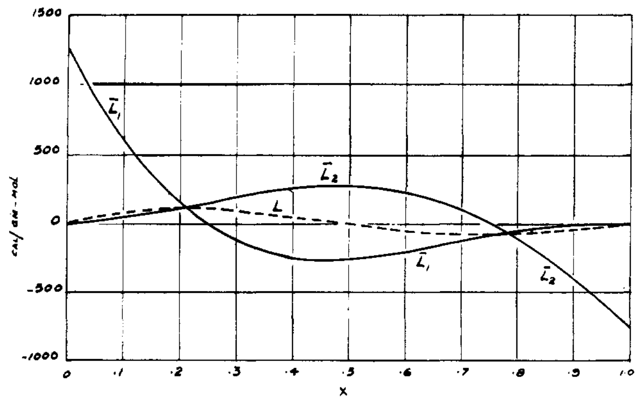

Figure 14. Partial and total heats of solution at the normal boiling points

The literature data cover the range 0 ° to 46 °C. while the atmospheric boiling points extend from 56° to 100 °C.; Equation 22 was used to extrapolate over this range.

Table IV gives the calculated values of the heat contents.

Heat Content of Saturated Vapor at 760 Mm. Enthalpy of the vapor of a pure component at a given temperature is the sum of the enthalpy of the liquid at boiling point, latent heat of vaporization at that temperature, and the amounts of superheat. Thus,

$$H_v = C_{p_1} \times t_B + \lambda + C_{p_v}(t - t_B)$$

where

C_{p_1} = specific heat of the liquid at t °C.

λ = latent heat of vaporization at t_B °C.

C_{p_v} = specific heat of vapor at t °C.

t_B = temperature of boiling of the liquid, °C.

The datum is taken as the enthalpy of the liquid at 0 °C. The effect of temperature on specific heat is neglected.

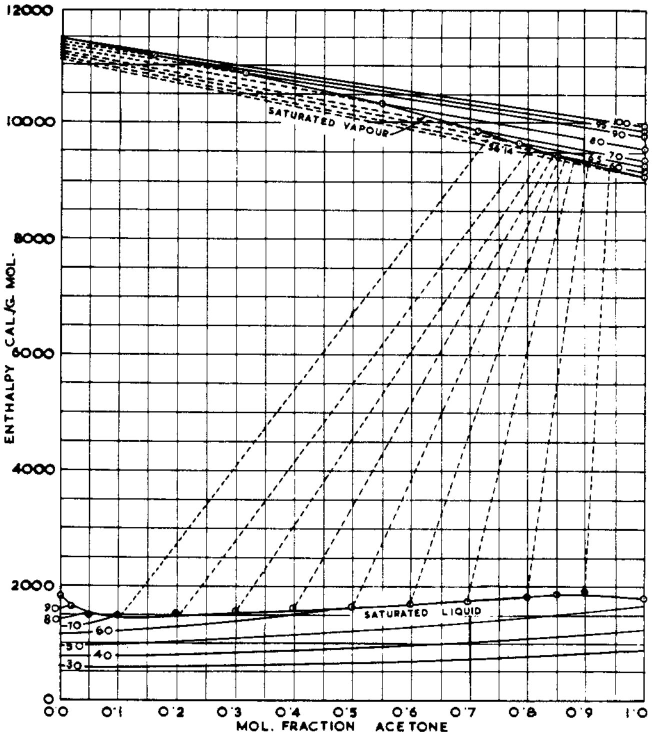

Figure 15. Enthalpies of saturated liquid and vapor, 760 mm.

From the data on specific heats of the liquid and vapor acetone and the enthalpies of water vapor which are available as a function of temperature, the termini of several isotherms are located along the $x_1 = 0$ and $x_1 = 1$ axes (Figure 15). The heats of solution of vapors being negligible at low pressures, the $H_v - x$ isotherms in the vapor region will be linear. Below the boiling point of water, the vapor phase is not stable for water-rich mixtures, but still the isotherms are drawn assuming lower pressures and that H_v is independent of pressure. The saturated vapor line is located thus. If t_1 and y_1 are the coordinates on the dew point line, the intersection of the t_1 isotherm with the ordinate at y_1 locates a point on the saturated vapor line.

Table IV gives the enthalpies of pure acetone and water vapors at the different isotherms chosen.

TABLE IV. Calculated Heat Content

Enthalpy of pure acetone liquid at 56.14 ° C., 1766 cal./gram mole.
Specific heat of pure acetone vapor, (25° to 110 °C.), 20.15 cal./gram mole/ °C.
Latent heat of vaporization of acetone (at 56.14 °C.), 7340 cal./gram mole.

Temp., °C.	Enthalpy of Acetone Vapor, Cal./Gram Mole: Superheat, cal./gram mole	Enthalpy of Acetone Vapor, Cal./Gram Mole: Enthalpy of vapor	Enthalpy of Water Vapor, Cal./Gram Mole
56.14	0	9106	11,190
60.0	78	9184	11,220
65.0	179	9285	11,257
70.0	279.0	9385	11,294
80.0	480.0	9586	11,367
90.0	681.0	9787	11,436
95.0	783.0	9889	11,470
100.0	884.0	9990	11,504

SUMMARY AND CONCLUSION

Two correlating methods that can be used with vapor-liquid equilibrium data have been studied for the system acetone-water. The isothermal activity coefficient data were expressed by a form of the Van Laar equation and the constants of the equation were correlated with temperatures. The isothermal and isobaric $x - y$ data were correlated by means of the Clark method; the constants were expressed as functions of temperature and pressure.

The isothermal activity coefficient correlation was used to calculate heats of solution and heat contents of liquid and vapor phases. The enthalpy concentration diagram of this system at 1 atmosphere of pressure is given.

With regard to the acetone-water system, a striking fact is the general lack of consistency in the data, particularly when an attempt is made to combine data of several different workers.

NOMENCLATURE

P = vapor pressure of acetone, mm. Hg
m_1, m_2, c_1, c_2 = constants of White's equation
M_1m, N_2m, C_1, C_2 = constants of Clark's equation
π = total pressure, mm. Hg
x = composition of liquid phase, mole fraction
y = composition of vapor phase, mole fraction
Subscripts 1, 2 = components, acetone and water, respectively
t and T = temperature, °C. and °K., respectively
R = gas constant, cal./gram mole, °K.
$\overline{L_1}$ = partial molal enthalpy of mixing of acetone, cal./gram mole
$\overline{L_2}$ = partial molar enthalpy of mixing of water, cal./gram mole
$L.$ = enthalpy of mixing of solution, cal./gram mole
C_{p_1} and C_{p_2} = specific heats of liquid acetone and water, respectively, cal./gram mole/ °C.
C_{p_V} = specific heat of acetone vapor, cal./gram mole/ °C.
H_L = enthalpy of liquid phase, cal./gram mole
H_V = enthalpy of vapor phase, cal./gram mole
P_r = vapor pressure of reference substance (Equation 19), atmospheres
γ_1 and γ_2 = activity coefficients
λ_1 and λ_2 = latent heats of vaporization of acetone and water, respectively, cal./gram mole

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Vapor Pressure of Sea Water Concentrates

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In the planning stage of a plant for the manufacture of salt by atmospheric evaporation of sea water, it was desired to calculate the rate of evaporation of bitterns at various densities. It was therefore necessary to know the vapor pressure of sea water at different stages of concentration. Values up to the crystallization point of sodium chloride are available in the literature (*1,8*), but data past this point, when the other constituents of sea salt begin to concentrate in the solution, are of special interest. Analyses by Dittmar (*5*) have shown that apart from variations in salinity, sea water from the major oceans of the world has a practically constant composition. It was therefore considered that correlation of vapor pressure with density would adequately express the data.

Sea water was obtained from about 10 miles off the coast in Cook Strait, New Zealand. The natural flow of ocean currents is sufficient to ensure that this water is substantially open-ocean water, uncontaminated by rivers and sewage. This water was concentrated in the laboratory. Once the crystallizing point was reached, the temperatures of the solution were not permitted to rise above the temperatures of measurement, thus ensuring that the various salts crystallized in the same sequence as they would in an evaporating pond. This was achieved by evaporating in a stream of cold air under an infrared lamp.

ISOPIESTIC METHOD

The isopiestic method of Robinson and Sinclair (*16*) was used in a simplified form for the vapor pressure measurements at 20° and 25°C. A solution of concentrated sea water, two widely differing solutions of sodium chloride, and a solution of sulfuric acid were put into small silica crucibles in a vacuum desiccator, and the whole was evacuated on a Geissler pump. The desiccator (suitably weighted with lead) was put in the thermostatic bath and left for 2 weeks, without any internal stirring or rocking as is normally employed to hasten equilibrium in the isopiestic method.

After 2 weeks, the densities of the four solutions were determined in a specific gravity bottle at 20°C.; the two sodium chloride solutions always were identical to 1 part in 1000. By using sulfuric acid as a reference material [Collins (*3*) for values at 20°C. and Stokes and Robinson (*18*) for 25°C.] the vapor pressure of the concentrated sea water could be ascertained. Values for the sodium chloride solutions showed good agreement with those of Olynyk and Gordon (*11*).

For the higher concentrations of sea water, with vapor pressures below that of saturated sodium chloride, an even simpler apparatus was employed. A 600-ml. lipless beaker was quarter filled with lead shot and bitumen, and a Petri dish with a glass division cemented across the middle was placed on the bitumen surface. Concentrated sea water was placed on one side of the division, and sulfuric acid on the other, a rubber bung and glass tap being used to seal the beaker. The evacuated beakers (with rubber caps over the tap ends) were again left in the water bath for 2 weeks, and the density of the solutions was then determined at 20°C. The sulfuric acid was always checked for the absence of chlorides at the conclusion of each experiment.

The results by the isopiestic method are estimated to be accurate to ± 0.1 mm.

STATIC METHOD

A static method of vapor pressure determination (*12*) was also used at 20°, 25°, and 30° (all thermostat temperatures to ±0.05°C.). The values obtained are estimated to be accurate to ±0.1 mm. at 30°C. but only ±0.3 mm. at 20°C.; the tendency is to obtain slightly high results, undoubtedly due to incomplete outgassing of the solutions, especially at the lower temperatures. The apparatus was checked with distilled water and solutions of sodium chloride (analytical reagent grade); for the latter the values for vapor pressure were those obtained by Olynyk and Gordon (*11*), who employed an elaborate static method, taking extreme precautions to out-gas their solutions.

While satisfactory agreement with the more accurate isopiestic values was obtained at 20° and 25°C., only the isopiestic results are quoted at these temperatures; at 30°C., where the static method is equally accurate, values obtained by this method are given.