

# Vapor Pressure in the System Acetone-Phosphoric Acid-Water

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The vapor pressures of both acetone and water were determined by a gas-chromatographic method for solutions at various temperatures which were established by a statistically designed pattern that covered the ranges encountered in both the extraction and distillation steps. The vapor-pressure data were fitted to the Clausius-Clapeyron equation,  $\ln P = -\Delta H/RT + B$ , over a temperature range of 26-99 °C. The heats of vaporization ( $\Delta H$ ) and intercepts ( $B$ ) for both acetone and water were correlated with composition by linear regression. The heats of vaporization for acetone and for total vapor increased as the phosphoric acid concentration increased and as the weight ratio of acetone to phosphoric acid decreased. Models of linear equations for  $\Delta H$  and  $B$  were derived to represent the vapor pressures. These equations were used to predict the heat of vaporization, and they were employed to construct the liquid-vapor phase diagram.

## Introduction

Fertilizer-grade phosphoric acid or wet-process phosphoric acid produced by acidulation of phosphate rock with sulfuric acid usually contains large amounts of metallic impurities such as Al, Fe, Mg, Ca, etc. (1). Since reserves of high-grade phosphate rock are limited, the phosphate industry is looking for a process for the recovery of phosphate from low-grade phosphate rock; this will result in even higher metallic impurities in the acid before a purification step. The high metal impurities in the product acid slowly precipitate as metallic phosphate complex compounds or ultimately result in lower grade phosphate fertilizers, neither of which is desirable.

One of the most promising processes to purify the wet-process acid is the acetone-ammonia extraction process (2, 3), in which the purified acid is accumulated in the acetone phase; and most of the impurities, together with small amounts of the acid, are collected in the bottom layer. The purified acid is produced by distillation of acetone from the acetone phase, and the acetone is recycled after condensation. Design of an efficient distillation process requires data on the variation of distillation temperature, vapor composition, and heat of vaporization with solution composition and the pressure used.

Vapor pressures in the acetone-water system have been reported by several workers (4-7), and the vapor pressure of phosphoric acid was extensively studied by Brown and Whitt (8) and others (9). However, no vapor-pressure data on the acetone-phosphoric acid-water system have been reported.

## Experimental Procedure

The apparatus consisted of a 2-L, round-bottom flask equipped with a heating mantle, a magnetic stirrer, a condenser, a vapor sampling line, a quartz thermometer (Dymec, Model 2801A), a gas chromatograph (Aerograph, Model A-350-B), and a peak integrator (Varian Aerograph, Model 485). The experimental apparatus is illustrated in Figure 1. The two condensers were connected in series; the first condenser was cooled with chilled water and the second was cooled with a dry ice-acetone mixture. Reagent-grade acetone and phosphoric

acid were used without further purification. Predetermined amounts of phosphoric acid, water, and acetone were weighed into the flask in sequence for each experiment so that the volume of the final solution was slightly more than 1 L. The pressure in the refluxing system was controlled with the vacuum pump and a controlled leakage through a needle valve, and it was measured by a U-tube mercury manometer. The pressure fluctuation during a measurement was maintained to within  $\sim 0.5$  mmHg. Vapor samples were withdrawn by evacuating the sampling valve and connecting tubes and then opening the stopcock to connect the flask with the gas chromatograph.

The gas chromatograph was operated under the following conditions: gas sampling valve temperature, 105 °C; column temperature, 120 °C; inlet and detector temperature, 150 °C; helium carrier gas flow rate, 30.6 cm<sup>3</sup>/min; column packing, 50-80-mesh silanized Porapak 2; column, 3 × 240 mm stainless steel. The detector signal was integrated with an electronic digital integrator, and the integrator and the detector were checked with standard acetone-water solutions (4) before each run.

Measurements were made for each solution composition by adjusting the pressure to the lowest value tested, 200 mmHg, and then applying heat to the solution to maintain a stable temperature and reflux rate. The solutions were stirred to prevent superheating, and a reflux time of 10 min was allowed for equilibrium to be established before vapor samples were taken. The sampling system was flushed with the vapor 3 times, and then six replicate samples were analyzed. The percent water and acetone in the vapor were determined from the integration printout of the gas chromatograph. The above procedure then was repeated for higher pressures, with incremental increases of 100 mmHg, until it reached 700 mmHg. The study was made for the composition of the solution ranging from 25 to 85 wt % phosphoric acid and for a weight ratio of acetone to phosphoric acid aqueous solution ranging from 0.125 to 2.

## Results

The boiling temperature and the vapor composition at each fixed pressure for each solution composition are listed in Table I as an average value of six replicate measurements. As postulated from previous data (8), there was no evidence that P<sub>2</sub>O<sub>5</sub> existed in the vapor phase in any test mixture. Therefore, the vapor phase was composed of acetone and water and very small amounts of air. The relative quantity of acetone and water in the vapor phase was evaluated from the gas chromatograph's peak area with appropriate weighting factors and presented as the mole fraction of acetone in Table I in the acetone-water gaseous mixture.

Since the logarithmic value of vapor pressure is proportional to  $1/T$  ( $T$  = absolute temperature), as illustrated in Figure 2, the integrated Clausius-Clapeyron equation

$$\ln P = -\Delta H/RT + B \quad (1)$$

was used to correlate the vapor pressure and the temperature of each composition, where  $P$  is the vapor pressure (mmHg),  $\Delta H$  is the heat of vaporization (cal/mol),  $B$  is a constant or intercept in Figure 2, and  $R$  is the gas constant (cal/(mol K)).

Table I. Vapor Composition and Distillation Temperature of Phosphoric Acid-Acetone-Water Solutions

expt no.	soln compn		total vapor pressure, mmHg											
	H <sub>3</sub> PO <sub>4</sub> concn, wt %	R <sup>a</sup>	200		300		400		500		600		700	
			temp, °C	y <sub>a</sub> <sup>b</sup>	temp, °C	y <sub>a</sub> <sup>b</sup>	temp, °C	y <sub>a</sub> <sup>b</sup>	temp, °C	y <sub>a</sub> <sup>b</sup>	temp, °C	y <sub>a</sub> <sup>b</sup>	temp, °C	y <sub>a</sub> <sup>b</sup>
1	25	0.25	37.86	0.9482	47.16	0.9334	54.05	0.9224	59.80	0.9169	64.54	0.9092	68.71	0.9036
2	25	1.00	28.63	0.9746	38.02	0.9652	45.10	0.9588	50.86	0.9532	55.72	0.9481	59.98	0.9417
3	40	0.125	45.89	0.9044	55.15	0.8957	62.10	0.8876	67.69	0.8785	72.53	0.8683	76.72	0.8572
4	40	0.50	33.10	0.9614	42.29	0.9559	49.15	0.9550	54.74	0.9511	59.50	0.9401	63.55	0.9318
5	40	2.00	26.13	0.9848	35.57	0.9782	42.56	0.9724	48.35	0.9664	53.28	0.9602	57.63	0.9545
6	55	0.125	52.81	0.9238	62.36	0.9113	69.43	0.8943	74.73	0.8832	78.93	0.8764	83.43	0.8673
7	55	0.25	42.75	0.9464	51.82	0.9331	58.87	0.9287	64.37	0.9199	69.18	0.9150	72.62	0.9130
8	55	0.50	35.22	0.9718	44.20	0.9629	50.82	0.9550	56.52	0.9498	61.17	0.9448	65.24	0.9367
9	55	1.00	28.95	0.9818	38.20	0.9744	45.28	0.9682	50.78	0.9668	55.76	0.9646	59.92	0.9565
10	55	2.00			34.84	0.9808	42.13	0.9772	47.82	0.9743	52.86	0.9675	57.09	0.9635
11	70	0.125	61.12	0.9090	70.72	0.8823	77.81	0.8777	83.31	0.8635	88.21	0.8542		
12	70	0.50	38.96	0.9749	48.02	0.9639	54.69	0.9586	60.18	0.9551	64.87	0.9513	68.93	0.9477
13	70	2.00			34.80	0.9848	41.71	0.9804	47.58	0.9789	52.47	0.9765	56.72	0.9753
14	85	0.25	67.58	0.9469	76.81	0.9326	83.92	0.9257	89.71	0.9201	94.55	0.9184	98.65	0.9167
15	85	1.00			40.37	0.9887	47.54	0.9858	53.31	0.9872	58.19	0.9861	62.40	0.9853

<sup>a</sup> Weight ratio acetone = acetone/(phosphoric acid + H<sub>2</sub>O). <sup>b</sup> Mole fraction of acetone in vapor phase.

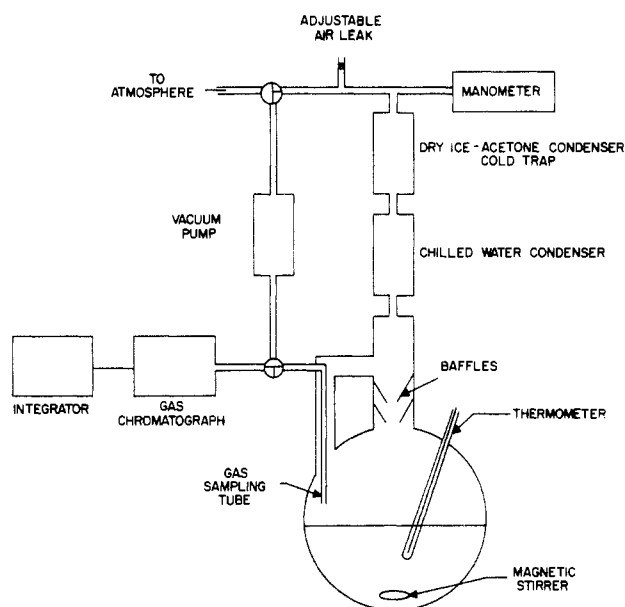


Figure 1. Experimental apparatus for the measurement of vapor pressure in the system acetone-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O.

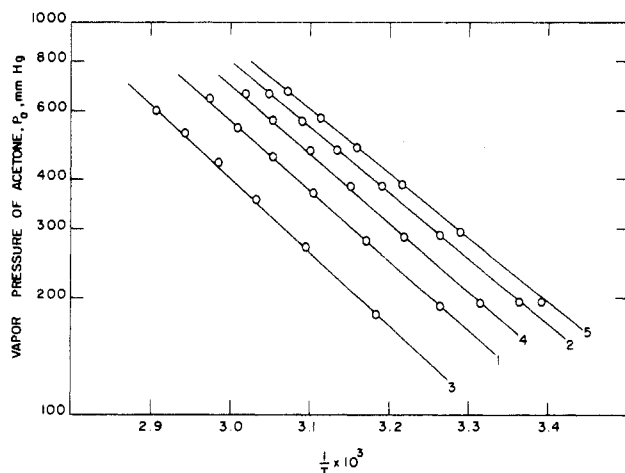


Figure 2. Relationship between acetone vapor pressure and temperature (numbers on curves denote experimental number in Table I).

The linear regression calculation was used to evaluate the heats of vaporization for total vapor ( $\Delta H_t$ ), acetone ( $\Delta H_a$ ), and water ( $\Delta H_w$ ) and their intercepts ( $B$ ) for the different compositions (Table II).

Table II. Heat of Vaporization and Intercept in Acetone-Phosphoric Acid-Water System

expt no.	heat of vaporization, cal/mol			intercept		
	total $\Delta H_t$	acetone $\Delta H_a$	water $\Delta H_w$	total $B_t$	acetone $B_a$	water $B_w$
	cal/mol	cal/mol	cal/mol			
1	8506.7	8254.6	12764.1	19.184	18.602	23.020
2	7981.2	7769.4	13124.7	18.609	18.231	23.538
3	9021.4	8645.1	11862.6	19.530	18.841	21.637
4	8425.7	8233.6	11993.0	19.144	18.793	21.699
5	7837.4	7643.8	14677.3	18.479	18.139	25.995
6	9525.8	9036.6	13844.1	19.996	19.165	24.079
7	9017.3	8846.8	12513.7	19.662	19.188	22.332
8	8647.1	8403.3	14055.1	19.414	18.988	24.684
9	8088.2	7937.1	13212.2	18.773	18.503	23.348
10	7698.9	7536.3	13614.5	18.282	17.999	23.961
11	9752.4	9225.6	13749.3	19.978	19.087	23.627
12	8877.8	8684.1	13844.5	19.614	19.276	24.004
13	7784.8	7697.4	12135.3	18.428	18.269	21.392
14	10115.4	9853.5	13696.4	20.243	19.799	22.651
15	8039.8	8014.0	10002.8	18.607	18.554	17.364

The correlation coefficients between observed values and the straight-line expression were better than 0.999 for all experiments, except for some of the water-vapor measurements which had large relative errors in the observed vapor pressure. The heat of vaporization for acetone and for total solution increased when phosphoric acid concentration,  $w$  (wt % of H<sub>3</sub>PO<sub>4</sub>), increased or when the weight ratio of acetone to phosphoric acid ( $R_a$ ) decreased, as shown in Figure 3. However, the heat of vaporization of water was somewhat erratic and did not show a simple relationship with the solution composition. The intercepts ( $B$ ) generally increased when the heat of vaporization increased. Therefore, the regression analysis for vapor pressure should treat the intercept, as well as the heat of vaporization, as a function of composition.

The data were analyzed by regression of  $\ln P$  vs.  $1/T$  according to eq 1 and by defining the heat of vaporization ( $\Delta H$ ) and the intercept ( $B$ ) with composition variables as follows:

$$\Delta H = F(x_a, x_w) = \sum_{j=0}^3 \sum_{i=0}^{3-i} l_j x_a^i x_w^j \quad (2)$$

$$B = G(x_a, x_w) = \sum_{j=0}^3 \sum_{i=0}^{3-i} m_j x_a^i x_w^j \quad (3)$$

where  $l_j$  and  $m_j$  are the regression constants and  $x_a$  and  $x_w$  are mole fractions of acetone and water, respectively. Stepwise regression analysis by the SAS computer program (10)

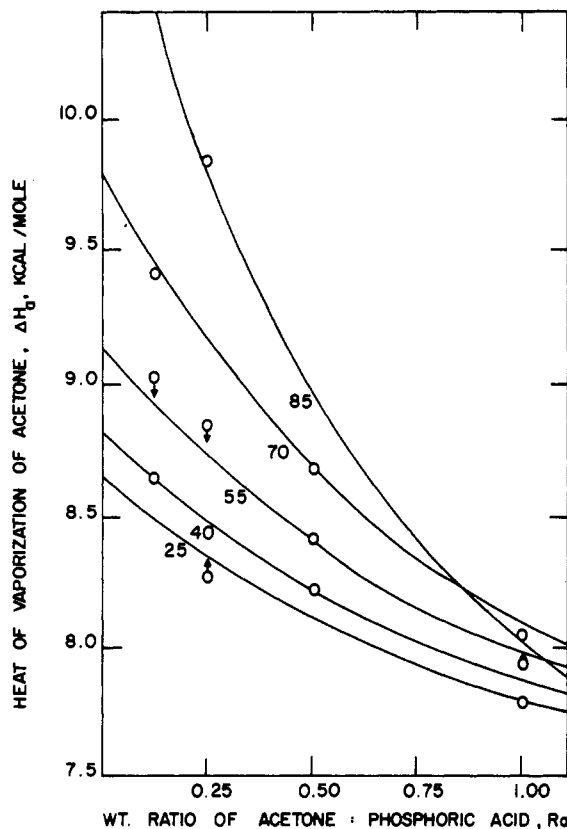


Figure 3. Comparison of calculated and observed heat of vaporization for acetone (solid lines are calculated values; numbers on curves denote acid concentration, %).

was used to select the  $l_j$  and  $m_j$  coefficients of 90% or more significance when eq 2 and 3 were substituted into eq 1 for regression using all of the data in Table I. The correlation coefficient of this model was 0.994, and the standard deviation was 3.5% for the total vapor pressure. The same treatment for acetone or water vapor pressure gave correlation coefficients of 0.994 and 0.991 and standard deviations of 3.5 and 8.6%, respectively.

Other composition sets were tested to improve the regression of eq 1 using eq 2 and 3, such as  $x_{ad} = x_a/(x_a + x_w)$  and  $x_w$ ,  $x_a$ , and  $x_p$  (mole fraction of  $H_3PO_4$ ) and  $x_w$  and  $x_p$ . The best result was obtained by using the  $x_{ad}$  and  $x_w$  variable set, which gave correlation coefficients of 0.998, 0.998, and 0.993 and standard deviations of 1.8, 1.8, and 7.8% for the total vapor, acetone, and water, respectively. This equation predicted the observed vapor pressure very accurately, but it did not predict the heats of vaporization accurately because of the high correlation of terms in the expressions for  $\Delta H$  and  $B$ .

The method that was adopted consisted of the stepwise regression for  $\Delta H$  from Table II using eq 2 and a subsequent stepwise regression for intercept terms using eq 1 and 3 with the  $\Delta H$  terms known. The best results for  $\Delta H$  expressions were obtained with the following independent variable sets:  $R_a$  and  $w$  for total vapor,  $x_a$  and  $x_w$  for acetone vapor, and  $w$  and  $R_3$  ( $R_3 = 3 - R_a$ ) for water vapor. The calculated heats of vaporization of acetone are compared with the observed values in Figure 3. Good agreement was obtained for the molar heats of vaporization of acetone and total vapor, but quite large deviations were noted in the heats of vaporization of water because of the relatively large error associated with the small amount of water vaporized. This could probably be improved for water by minimizing  $\sum (P_w - \hat{P}_w)^2$  rather than  $\sum (\ln P_w - \ln \hat{P}_w)^2$ , where  $\hat{P}_w$  is the calculated pressure of water by eq 1, because the minimum sums of squares by the logarithmic ex-

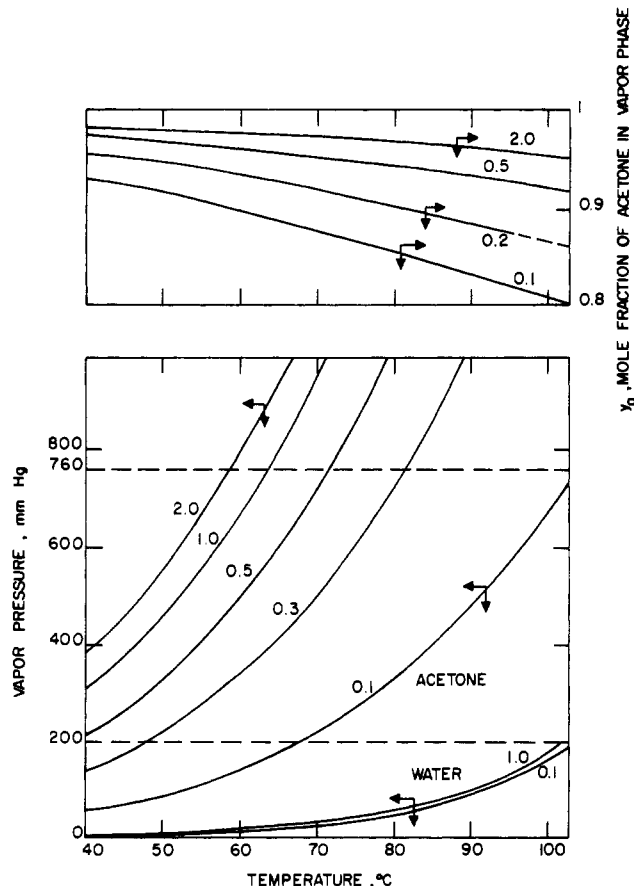


Figure 4. Calculated vapor pressure of acetone and water at different temperatures for 70% phosphoric acid (numbers on curves denote weight ratios of acetone to acid,  $R_a$ ).

pression gives too much weight to the low water vapor pressure,  $P_w$ .

The final models are as follows:

$$\ln P_t = -(a_0 + a_1 R_a + A_2 w^2 + a_3 w^2 R_a + a_4 w R_a^2) / RT + (a_{10} + a_{11} R_a + a_{12} w + a_{13} w^2 + a_{14} R_a^2 + a_{15} w R_a + a_{16} w R_a^2 + a_{17} w^3 + a_{18} R_a^3) \quad (4)$$

$$\ln P_a = -(b_0 + b_1 x_a + b_2 x_a x_w + b_3 x_w^2 + b_4 x_a^3 + b_5 x_w^3) / RT + (b_{10} + b_{11} x_a + b_{12} x_w + b_{13} x_a x_w + b_{14} x_a^2 + b_{15} x_w^2 + b_{16} x_a^2 x_w + b_{17} x_a x_w^2 + b_{18} x_a^3 + b_{19} x_w^3) \quad (5)$$

$$\ln P_w = -(c_0 + c_1 w R_3 + c_2 w^2 R_3 + c_3 w^2 + c_4 w^3) / RT + (c_{10} + c_{11} w R_3 + c_{12} R_3^2 + c_{13} w^2 R_3 + c_{14} w R_3^2 + c_{15} w^2 + c_{16} w^3) \quad (6)$$

where  $P_t$ ,  $P_a$ , and  $P_w$  are the vapor pressures of total, acetone, and water, respectively (mmHg). The correlation coefficient between observed and calculated values for total vapor pressure was 0.997, and the standard deviation was 3.33%. Equivalent values for acetone were 0.997 and 2.78% and for water were 0.998 and 8.65%. The coefficients for the equations are listed in Table III.

Because of the sequential regression derivation, eq 4-6 represent the total and partial vapor pressures of water and acetone, as well as their molar heats of vaporization in the system  $H_3PO_4$ -acetone- $H_2O$ . As an example, Figure 4 shows the acetone and water partial pressures calculated from eq 5 and 6 for 70% phosphoric acid and various contents of ace-

Table III. Constants for Eq 3-5

$a_0 = 8678.681$	$b_0 = 13099.32$	$c_0 = 15676.73$
$a_1 = -1046.576$	$b_1 = -12183.08$	$c_1 = -104.4268$
$a_2 = 0.314494$	$b_2 = 6042.103$	$c_2 = 1.760517$
$a_3 = -0.401023$	$b_3 = -11980.20$	$c_3 = 2.025467$
$a_4 = 12.46383$	$b_4 = 7396.160$	$c_4 = -0.044726$
$a_{10} = 19.34818$	$b_5 = 7400.94$	$c_{10} = 27.0854$
$a_{11} = 0.69229$	$b_{10} = 9.5867$	$c_{11} = -0.15412$
$a_{12} = -0.030513$	$b_{11} = 41.7305$	$c_{12} = 0.078886$
$a_{13} = 0.0010815$	$b_{12} = 37.4542$	$c_{13} = 0.0027137$
$a_{14} = -2.152017$	$b_{13} = -71.3246$	$c_{14} = -0.0034186$
$a_{15} = -0.000184$	$b_{14} = -76.4477$	$c_{15} = 0.0032989$
$a_{16} = 0.002676$	$b_{15} = -48.3909$	$c_{16} = -0.00007316$
$a_{17} = -0.00000679$	$b_{16} = 43.8592$	
$a_{18} = 0.800478$	$b_{17} = 29.5312$	
	$b_{18} = 46.9227$	
	$b_{19} = 20.0860$	

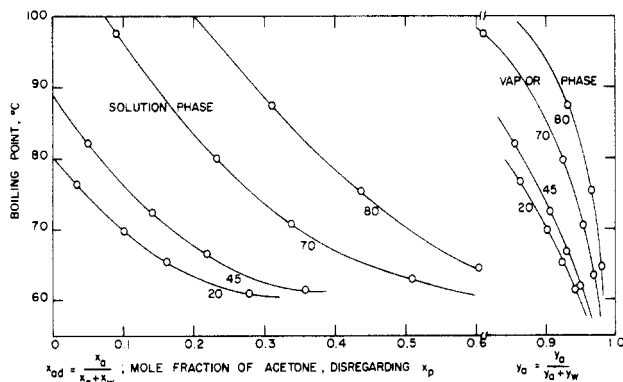


Figure 5. Change of acetone mole fraction from solutions to vapor phase at 1 atm for different acid concentrations (numbers on curves denote acid concentration, %).

tone. The total vapor pressure can be obtained by adding the two partial pressures at each  $R_a$  value, or it could be calculated from eq 4. The boiling point at any fixed total pressure and composition of liquid can be obtained by solving eq 3 for the temperature,  $T$ , or by computing graphically where the sum,  $P_a + P_w$ , intersects a given isobar, as illustrated in Figure 4 by the dotted lines for 760 and 200 mmHg. The mole fractions of acetone in the vapor phase ( $y_a$ ) also are shown by the upper lines as a function of temperature and the acetone content for 70%  $H_3PO_4$ . Similar graphs can be drawn for other phosphoric acid concentrations.

The mole fractions of acetone with respect to water in solution  $x_a/(x_a + x_w)$  and in the vapor  $y_a/(y_a + y_w)$  are thus calculated and presented in Figure 5 for 760 mmHg total pressure as a function of the boiling temperature for different acid concentrations containing various amounts of acetone. Acetone is preferentially volatilized, particularly at low temperature. For example, 70% phosphoric acid mixed with acetone at a weight ratio 1:1 starts boiling at 63 °C under atmospheric pressure, and its vapor phase contains 95% (vol) or 98% (wt) acetone; thus, only 2% (wt) of the condensate is water, and the acid concentration changes very little during the distillation. At the reduced pressure of 200 mmHg, the acetone mole fraction in the vapor phase is increased slightly over that at 760 mmHg, and the boiling temperature is decreased  $\sim 30$  °C. Some beneficial effect might be realized by operating the distillation at reduced pressure, such as lower heat requirements.

The change in the composition of the solution during a distillation step can be calculated by utilizing Figure 5 with incremental computation. A sample calculation for atmospheric distillation of 20, 45, 70, and 80%  $H_3PO_4$ , each mixed with twice its weight of acetone, is shown in Figure 6. The acid concentration does not change noticeably during the early part of the distillation, but it increases gradually so that the final acid

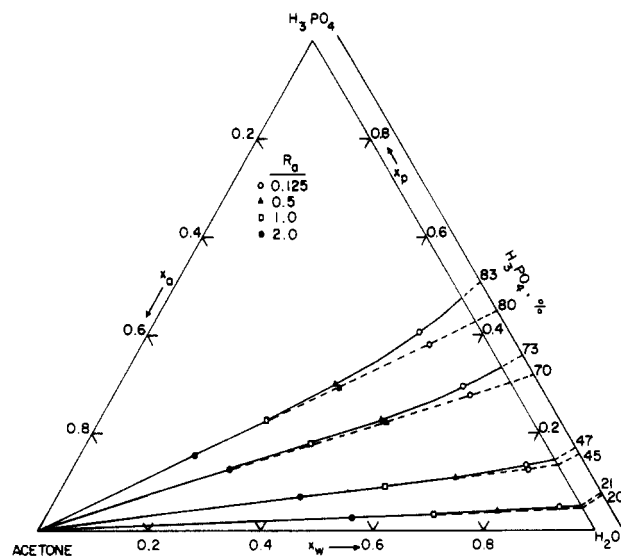


Figure 6. Solution composition change during distillation of acetone from acetone-phosphoric acid-water at 1 atm.

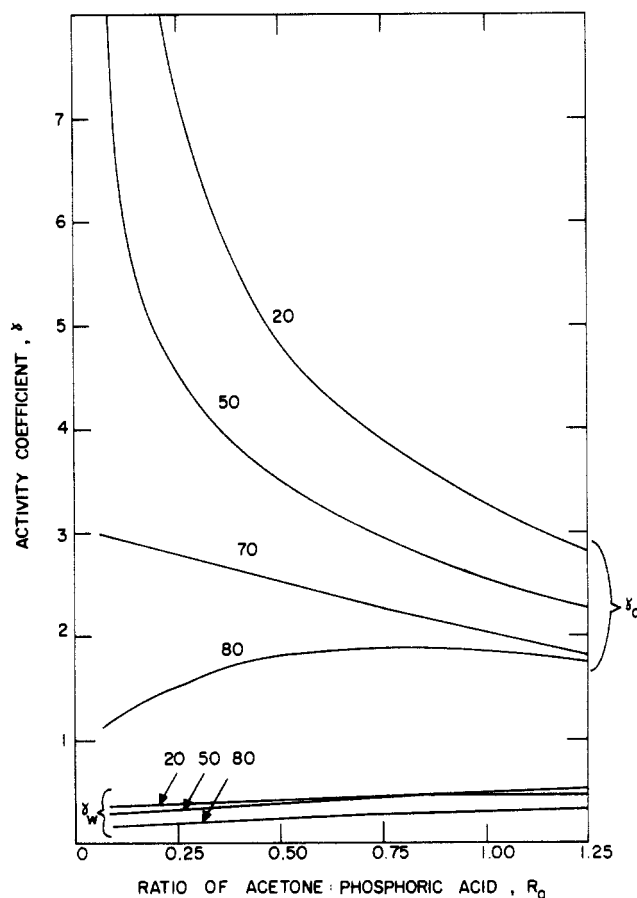


Figure 7. Activity coefficient change of acetone and water depending on  $R_a$  at 70 °C (numbers on curves denote acid concentration, %).

concentration is only a few percentage points higher at the end of acetone distillation. Further heating after acetone distillation will eventually evaporate the remaining water at a higher temperature to produce more concentrated acid as desired.

As a convenient reference table (Table IV), the molar heats of vaporization and the intercepts of eq 1 for both acetone and water were calculated for wide concentrations of acid containing various amounts of acetone by using eq 5 and 6. Also, the partial pressures of acetone and water in mmHg at 40, 60, and 80 °C were evaluated and are listed in Table IV. The activity coefficients of acetone,  $\gamma_a$ , and water,  $\gamma_w$ , in the so-

Table IV. Calculated Values: Heats of Vaporization, Intercepts, Vapor Pressures, and Activity Coefficients at Different Temperatures in the Acetone-Phosphoric Acid-Water System

H <sub>3</sub> PO <sub>4</sub> concn, %	R <sup>a</sup>	40 °C										60 °C										80 °C									
		$\Delta H_{vap}^b$ cal/mol	B <sub>a</sub> <sup>c</sup>	$\Delta H_{wv}^b$ cal/mol	B <sub>w</sub> <sup>c</sup>	P <sub>a</sub> <sup>d</sup>	P <sub>w</sub> <sup>d</sup>	$\gamma_a^e$	$\gamma_w^e$	P <sub>a</sub> <sup>d</sup>	P <sub>w</sub> <sup>d</sup>	$\gamma_a^e$	$\gamma_w^e$	P <sub>a</sub> <sup>d</sup>	P <sub>w</sub> <sup>d</sup>	$\gamma_a^e$	$\gamma_w^e$	P <sub>a</sub> <sup>d</sup>	P <sub>w</sub> <sup>d</sup>	$\gamma_a^e$	$\gamma_w^e$										
20	0.1	8480.2	18.721	12114.6	22.117	162.95	14.15	12.209	0.277	369.26	45.53	13.240	0.331	762.75	128.33	14.226	0.392														
20	0.5	8074.3	18.564	12668.3	22.893	267.37	12.63	4.579	0.283	582.64	42.86	4.775	0.356	1162.4	126.67	4.956	0.442														
20	1.0	7773.5	18.276	13360.5	23.868	325.04	11.00	3.219	0.285	688.06	39.93	3.261	0.383	1337.9	125.22	3.298	0.506														
20	1.6	7580.2	18.011	14191.1	25.045	340.29	9.39	2.448	0.283	707.02	36.94	2.434	0.412	1352.2	124.36	2.421	0.584														
30	0.1	8557.8	18.759	11801.9	21.555	149.50	13.32	10.148	0.270	341.34	41.60	11.087	0.313	709.76	114.16	11.993	0.361														
30	0.5	8132.7	18.639	12421.2	22.478	262.44	12.40	4.125	0.291	575.13	41.10	4.326	0.358	1153.2	118.94	4.512	0.436														
30	1.0	7817.8	18.340	13195.4	23.622	322.88	11.22	2.970	0.309	686.41	40.07	3.021	0.408	1339.8	123.88	3.068	0.531														
30	1.6	7616.3	18.065	14124.4	24.979	339.08	9.79	2.290	0.316	706.97	38.26	2.285	0.458	1356.3	128.06	2.280	0.645														
40	0.1	8672.6	18.828	12110.3	21.909	133.12	11.57	8.098	0.245	307.33	37.20	8.946	0.292	645.4	104.83	9.773	0.347														
40	0.5	8214.9	18.745	12654.4	22.763	255.75	11.33	3.659	0.283	564.93	38.42	3.868	0.355	1140.7	113.42	4.063	0.441														
40	1.0	7874.2	18.422	13334.5	23.805	319.97	10.77	2.718	0.319	683.94	38.97	2.780	0.428	1341.4	121.93	2.836	0.563														
40	1.6	7657.2	18.129	14150.7	25.016	338.49	9.74	2.137	0.343	708.53	38.15	2.140	0.498	1364.1	128.02	2.144	0.703														
50	0.1	8843.9	18.938	12771.5	22.741	112.90	9.19	6.072	0.207	264.99	31.49	6.820	0.263	564.66	93.90	7.560	0.329														
50	0.5	8327.8	18.889	13099.6	23.308	246.27	9.56	3.177	0.258	549.94	33.84	3.395	0.338	1121.3	103.78	3.600	0.437														
50	1.0	7942.2	18.519	13509.6	23.976	316.05	9.65	2.462	0.315	679.99	35.52	2.534	0.429	1341.4	112.83	2.601	0.573														
50	1.6	7699.5	18.199	14001.6	24.717	339.15	9.18	1.992	0.361	712.81	35.44	2.003	0.516	1377.3	117.39	2.013	0.719														
60	0.1	9103.1	19.104	13517.2	23.612	87.85	6.62	4.106	0.162	211.41	24.40	4.728	0.221	460.60	77.54	5.359	0.296														
60	0.5	8478.3	19.072	13488.3	23.676	232.20	7.39	2.668	0.222	526.11	27.16	2.893	0.302	1086.6	86.12	3.108	0.403														
60	1.0	8016.9	18.622	13452.2	23.699	310.73	8.02	2.201	0.297	673.38	29.35	2.283	0.403	1336.9	92.76	2.358	0.536														
60	1.6	7735.4	18.266	13408.8	23.643	342.22	8.13	1.859	0.370	721.76	29.63	1.876	0.499	1398.9	93.31	1.891	0.661														
70	0.1	9500.4	19.323	14078.9	24.083	57.77	4.30	2.293	0.119	144.45	16.73	2.744	0.172	325.59	55.78	3.217	0.241														
70	0.5	8666.8	19.276	13552.2	23.426	210.43	5.20	2.121	0.183	485.54	19.21	2.342	0.250	1019.1	61.24	2.557	0.336														
70	1.0	8082.3	18.703	12893.9	22.532	303.47	6.13	1.936	0.273	661.82	21.25	2.020	0.350	1321.3	64.03	2.098	0.444														
70	1.6	7748.7	18.310	12103.9	21.354	349.90	6.71	1.746	0.374	738.90	21.57	1.765	0.445	1433.7	60.76	1.781	0.528														
80	0.1	10109.3	19.505	14188.3	23.715	26.05	2.50	0.850	0.085	69.08	9.81	1.079	0.124	164.04	33.03	1.333	0.176														
80	0.5	8864.9	19.415	13023.0	22.120	175.81	3.30	1.525	0.150	413.48	11.58	1.716	0.195	882.67	35.27	1.905	0.249														
80	1.0	8094.0	18.689	11566.5	20.039	293.53	4.27	1.666	0.254	640.87	13.04	1.740	0.287	1280.77	35.06	1.809	0.325														
80	1.6	7705.3	18.287	9816.6	17.413	366.65	5.13	1.669	0.391	771.05	13.22	1.679	0.373	1490.54	30.62	1.689	0.364														
90	0.1	10967.4	19.065	13577.1	22.069	4.22	1.29	0.108	0.069	12.17	4.76	0.149	0.095	31.09	15.22	0.198	0.127														
90	0.5	8929.3	19.152	11632.4	19.319	121.90	1.87	0.885	0.142	288.48	5.75	1.003	0.162	619.23	15.54	1.119	0.184														
90	1.0	7934.5	18.385	9201.5	15.779	279.88	2.70	1.391	0.281	601.73	6.55	1.431	0.253	1186.25	14.40	1.468	0.233														
90	1.6	7534.3	18.105	6284.4	11.379	402.46	3.60	1.654	0.495	832.50	6.60	1.638	0.336	1585.97	11.29	1.623	0.242														

<sup>a</sup> Acetone weight ratio: acetone/phosphoric acid. <sup>b</sup> Molar heat of vaporization, cal/mol. Subscripts a and w denote acetone and water, respectively. <sup>c</sup> Intercept of straight line in  $\ln P$  vs.  $1/T$  plot. Subscripts a and w denote acetone and water, respectively. <sup>d</sup> Vapor pressure, mmHg. Subscripts a and w denote acetone and water, respectively. <sup>e</sup> Activity coefficient based on Raoult's law:  $P_a^0 = \gamma_a X_a$ . Subscripts a and w denote acetone and water, respectively.

Table V. Latent Heat Requirement for Acetone Distillation at 760 mmHg

acid concn, %	$R_a$ change	heat required, kcal/kg ( $H_3PO_4 + H_2O$ )	av temp, °C	final acid concn, %
20.0	3 → 2	132	56	20.0
	2 → 1	132	58	20.0
	1 → 0	140	70	21.0
45.0	3 → 2	132	56	45.0
	2 → 1	133	59	45.1
	1 → 0	142	72	47.1
70.0	3 → 2	132	56	70.0
	2 → 1	136	60	70.6
	1 → 0	150	80	72.9
80.0	3 → 2	133	56	80.0
	2 → 1	140	61	80.6
	1 → 0	174	87	82.9

lution phase then were calculated from deviations from Raoult's Law by eq 7, where  $P^0$  (mmHg) is the vapor pressure of the

$$\gamma_a = P_a / (x_a P_a^0) \quad \gamma_w = P_w / (x_w P_w^0) \quad (7)$$

pure component at a given temperature, which is obtained from recent data (11, 12). The activity coefficients of acetone ( $\gamma_a$ ) is always larger than unity, except at very high acid concentration and very low values of  $R_a$ ; it becomes quite large at low acid concentration and low  $R_a$ . This high activity coefficient of acetone is expected because of its low boiling point compared with that of water in phosphoric acid. However, the low  $\gamma_a$  value at high acid concentration with small amounts of acetone indicates the relative difficulty of complete distillation of acetone from the concentrated acid because it may form a relatively strong bond between acetone and phosphoric acid molecules. When the solution contained a large quantity of acetone, the  $\gamma_a$  value converged to a value of  $\sim 2.5$  for all acid concentrations. The activity coefficient of water is usually less than

0.5 and decreases slightly as  $R_a$  decreases and as the acid concentration increases. These values of  $\gamma_a$  also indicate the preferential distillation of acetone from the solution since acetone has a larger activity coefficient than water. Figure 7 shows the activity coefficients of acetone and water at 70 °C, and similar patterns are predicted at other temperatures.

The overall latent heat requirements for the distillation of acetone from phosphoric acid of different concentrations are calculated from the  $\Delta H$  values from eq 4 or a combination of eq 5 and 6 (Table V). The heat of vaporization for the solution at large  $R_a$  values is approximately the same as the heat of vaporization of pure acetone (7.64 kcal/(mol of acetone)), regardless of the phosphoric acid concentration, since most of the distillate is acetone, as indicated by Figure 5. The heat of vaporization gradually increases as  $R_a$  decreases and phosphoric acid concentration increases. The average boiling points of the solutions, within the  $R_a$  range listed, increase with the increase of phosphoric acid concentration.

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## Second Virial Coefficients of Propane-Isomeric Hexane Mixtures

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The compressibilities of five isomeric hexanes (*n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane) as well as their mixtures with propane were measured between 369.7 and 508 K. Second virial coefficients were calculated from the compressibility measurements and are presented in this paper. The results agree with values calculated by using the Tsonopoulos-Pitzer-Curl correlation.

#### Introduction

The thermodynamic properties of nonideal gases and vapors may easily be calculated from a knowledge of the virial coefficients and their dependence on temperature. For calculations at low or moderate pressures, the effect of vapor-phase non-

idealities can reliably be estimated by using only the second virial coefficient. The proper accounting of these nonidealities is of great importance in, for example, the correlation of vapor-liquid equilibria. An advantage of expressing gas-phase nonidealities by means of the virial equation is that there is a theoretical relationship between the virial coefficients and the intermolecular potential function. Thus the second virial coefficient provides a direct link between experimental measurements, on the one hand, and intermolecular forces, on the other.

The aims of this work were to obtain second virial coefficient data for binary mixtures of propane with the isomers of hexane, so that the effect of the shape of the molecules on intermolecular forces in mixtures could be studied, and also to see whether the currently available correlations for second virial coefficients are able to predict the effects of shape on the properties of mixtures.

Many correlations of second virial coefficients have appeared in the chemical engineering literature. Among the more recent ones are those of Tsonopoulos (1), Hayden and O'Connell (2),

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