Vapor-Liquid Equilibrium Data for Systems of Acetone-Methanol-Isopropanol

D. C. FRESHWATER
Department of Chemical Engineering, University of Technology, Loughborough, England
K. A. PIKE
Imperial Smelting Corporation Ltd., Avonmouth, Nr. Bristol, England

Vapor-liquid equilibrium data for the binary and ternary systems composed of acetone, methanol, and isopropanol are presented for an isothermal condition of 55° C. and also an isobaric condition of 760 mm. of Hg. The experimental data have been used to extend the use of isothermal solutions of ternary predicting equations to isobaric situations by use of temperature correlations. Comparative results for the Van Laar, Margules, and Redlich and Kister equations show that the last named gives the best correlation with root mean square deviations of 0.0058 for the isothermal data and 0.0047 for the isobaric data.

THE VAPOR-LIQUID equilibrium data for the binary and ternary systems composed of these three components have been studied at an isothermal condition of 55° C. and also at an isobaric condition of 760.00 mm. of Hg. The majority of these systems have not been investigated previously at these or at any other conditions.

Experimental determination of the vapor-liquid equilibrium has been made using a modified Ellis (*10, 22*) equilibrium still. The samples of liquid and vapor phases were analyzed by a gas chromatograph linked directly to a data-logging system. This method gave the analysis for each component present in the system thus obviating the need for interpolation on three coordinate graphs, which is a requirement of older methods. The method was used for binary and ternary systems but can be easily extended to handle quaternary or higher order systems. A detailed description of the method which gave analysis to an accuracy of ±0.05 mole % is given elsewhere (*22*). The physical properties after purification of the materials used in this investigation are shown in Table I.

The binary systems investigated, using the Ellis equilibrium still, were acetone-methanol and methanol-isopropanol at an isothermal state of 55° C., and acetone-isopropanol was investigated at an isothermal state of 55° C. and an isobaric state of 760.00 mm. of Hg. Data of sufficient accuracy and thermodynamic consistency existed for the isobaric condition of 760.00 mm. of Hg for acetone-methanol (*1, 2*) and methanol-isopropanol (*1, 4*).

The ternary system of acetone-methanol-isopropanol was determined at 55° C. and at 760.00 mm. of Hg. The system has been experimentally determined at 760.00 mm. of Hg on a previous occasion (*1*) but these results do not give adequate coverage of the whole ternary diagram (*22*).

THERMODYNAMIC CONSISTENCY OF RESULTS

For the binary systems, the Herington (*12, 14*), Redlich and Kister (*23*) method and the qualitative observation methods of Lu (*18, 19*) were used to test the thermodynamic consistency of experimental data. The thermodynamic consistency of ternary data was estimated by means of the test proposed by McDermott and Ellis (*21*). All of these tests require a knowledge of the activity coefficients of the experimental data, and the equation proposed by Scatchard and Raymond (*25*) has been used in this investigation—due account being taken of the vapor pressure and second virial coefficient data involved.

BINARY DATA

The results of applying the area consistency test of Herington (*12, 14*) and Redlich and Kister (*23*) are summarized in Table II for the isothermal data. In general the limits for the ratio of areas above and below the log $(\gamma_1/\gamma_2) = 0$ line proposed by Ellis and Bourne (*11*) at 0.95 to 1.05 for consistent data are satisfied.

The methanol-isopropanol system is indicated as being slightly inconsistent but the experimental log γ *vs.* liquid composition data indicated little divergence from ideality, which in consequence means that the ratio of two very small areas was being taken. In these circumstances, and supported by the visual observations of the Lu (*18, 19*) tests, the data are considered to be thermodynamically consistent.

The Herington (*13*) test was used for testing the isobaric data determined experimentally in this investigation for acetone-isopropanol and also data for the two other systems which are used later in correlating studies. The Lu (*18, 19*) tests also have been used to check the data. The lack of heat of mixing data prevented the use of other tests which require detailed heat of mixing data. For acetone-methanol, the data of Amer, Paxton, and Van Winkle (*2*) and of Allen and Pike (*1*) were tested by these methods, and as the two sets of data did not have any major divergences, they were combined and tested. The acetone-isopropanol system was investigated by Allen and Pike (*1*) and by Choffe and Asselineau (*8*) at 760.00 mm. of Hg previous to the present investigations. When tested

Table I. Physical Properties of the Materials

Component	Refractive Index at 20° C.	Specific Gravity at 20° C.	Boiling Point ° C., at 760.00 Mm. of Hg
Acetone	1.3590	0.7902	56.25
Methanol	1.3287	0.7915	64.45
Isopropanol	1.3775	0.7850	82.30

Table II. Isothermal Binary Consistency Test Results

Data at 55° C.	Ratio of Areas
Acetone-methanol	1.012
Acetone-isopropanol	1.011
Methanol-isopropanol	0.93

for consistency, the data of the two previous investigations did not agree in the middle composition range. The results of the present investigation confirmed those of Allen and Pike (*1*).

Methanol-isopropanol at 760.00 mm. of Hg has been investigated by Ballard and Van Winkle (*4*) and Allen and Pike (*1*). The data contained little deviation from ideality, and the two sets of data were comparable. The Herington test was applied to the two sets of data combined, and the data were thermodynamically consistent. The isobaric data available indicated that the system has negative deviations from ideality, while the isothermal data showed slight positive deviations from ideality.

TERNARY DATA

Both the isothermal and the isobaric data have been tested for thermodynamic consistency using the McDermott and Ellis (*21*) test. The data for the ternary system at 55° C. contained few inconsistent points, and they have been discarded for subsequent correlating exercises. The isobaric data of Allen and Pike (*1*), besides being confined to a low acetone concentration also contained more inconsistent points than that of the present investigation. Again, in the subsequent correlating exercises inconsistent data has been discarded.

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA

The data determined in the present investigation are given as a tabular presentation together with the constants of the correlating equation which gave the best fit. The three equations considered (Tables III and IV) were those of Van Laar (*27*) Margules (*20*), and Redlich and Kister (*23*); for the ternary systems (Table V) the Wohl (*29, 30*) solution of the first two equations was used. Temperature correlations of vapor pressure data and virial coefficient data have been used for the isobaric data, and these are described later.

DETERMINATION OF CONSTANTS IN CORRELATING EQUATIONS

For both the testing of the thermodynamic consistency of experimental data and for determining the constants of correlating equations, the experimental activity coefficients must be known accurately. For isothermal conditions, the use of the Scatchard and Raymond equation for activity coefficient determination is comparatively straight forward. Under isobaric conditions, however, some of the terms in the equation, notably P_1^0, vapor pressure, $B11$, second virial coefficient, and $B12$, mixed second virial coefficient vary considerably with temperature, and temperature correlations were necessary for these three terms. The molar volume, V, also varies with temperature but the variation is slight, and the values of V compared with $B11$, from which they are subtracted in the equation, are small ($B11 : V \doteq 20 : 1$), and an allowance need not be made for variations of molar volume, V, with temperature. In drawing up temperature correlations for vapor pressure and second virial coefficients, some discrepancies in the published data were observed.

SECOND VIRIAL COEFFICIENTS

The three components acetone, methanol, and isopropanol are all strongly polar, and limited virial coefficient data for these compounds are available. The sources of data did not always agree on values of the second virial coefficient, and in these cases the more closely grouped values were taken and averaged. The divergence in values of second virial coefficient is believed to occur because

Table III. Isothermal Binary Data at 55° C.

Acetone Mole Fraction X_1 Liquid Phase	Acetone Mole Fraction Y_1 Vapor Phase	Pressure, Mm. of Hg
	Acetone-Methanol	
0.0287	0.0647	542.17
0.0570	0.1295	564.61
0.0644	0.1407	569.56
0.0858	0.1848	581.45
0.1046	0.2190	592.15
0.1357	0.2637	610.13
0.1452	0.2694	618.98
0.1663	0.3055	628.16
0.2173	0.3633	650.74
0.2390	0.3863	657.70
0.2787	0.4184	675.68
0.3579	0.4779	699.07
0.4050	0.5135	712.65
0.4480	0.5512	722.76
0.5052	0.5844	732.37
0.5432	0.6174	738.49
0.6332	0.6772	748.61
0.6538	0.6849	752.18
0.6605	0.6926	749.65
0.6945	0.7124	752.11
0.7327	0.7383	753.53
0.7525	0.7618	753.85
0.7752	0.7729	757.52
0.7922	0.7876	757.97
0.9080	0.8959	749.10
0.9088	0.8963	750.31
0.9197	0.8941	750.47
0.9448	0.9336	748.52
	Acetone-Isopropanol	
0.9214	0.9629	707.37
0.8569	0.9240	684.21
0.7338	0.8729	644.62
0.7216	0.8617	637.84
0.6084	0.8098	602.20
0.5234	0.7655	563.06
0.4314	0.7284	533.87
0.3879	0.6995	517.54
0.2687	0.6024	456.40
0.2353	0.5722	442.91
0.1591	0.4762	390.23
0.0971	0.3625	331.59
0.0642	0.2777	299.50
0.0237	0.1166	257.97
	Methanol-Isopropanol	
0.9529	0.9816	494.80
0.9232	0.9636	488.41
0.8854	0.9479	478.39
0.8432	0.9191	466.47
0.7946	0.8915	460.54
0.7372	0.8596	445.49
0.6983	0.8330	432.97
0.5990	0.7693	402.85
0.5310	0.7189	383.30
0.4682	0.6664	364.13
0.3986	0.6027	346.22
0.3498	0.5460	330.89
0.2739	0.4626	312.66
0.2314	0.4070	297.66
0.2107	0.3711	287.66
0.1902	0.3428	289.25
0.1638	0.3062	273.03
0.1069	0.2056	258.93
0.0822	0.1702	250.90
0.0451	0.1120	247.02

System	Equation Giving Best Correlating Fit	First Constant	Second Constant
Acetone-Methanol	Redlich and Kister	+0.2935	−0.0152
Acetone-Isopropanol	Van Laar or the Redlich and Kister	+0.2883 +0.2871	+0.2770 −0.0117
Methanol-Isopropanol	Van Laar	+0.0268	+0.0474

Table IV. Isobaric Binary Data at 760.00 Mm. of Hg

Acetone-Isopropanol

Acetone Mole Fraction X_1 Liquid Phase	Acetone Mole Fraction Y_1 Vapor Phase	Temp., ° C.
0.9249	0.9614	56.78
0.7691	0.8873	58.75
0.6077	0.8081	61.19
0.4629	0.7242	63.80
0.4215	0.6974	64.60
0.3997	0.6860	65.01
0.2486	0.5261	69.32
0.1927	0.4525	71.63
0.1468	0.3793	73.41
0.1080	0.3018	75.41
0.0359	0.1135	79.78

Equation Giving Best Correlating Fit	First Constant	Second Constant
Redlich and Kister	+0.1977	+0.0065

in some literature references other order virial coefficients have also been considered in the fitting of an equation of state. Authors have not always stated where more than one virial coefficient has been considered (Table VI).

MIXED SECOND VIRIAL COEFFICIENTS

In the binary and ternary forms of the equation for experimental activity coefficients, the interaction parameter δ occurs. This parameter is a function of the mixed second virial coefficient as well as the second virial coefficients of the pure components. Experimental data on mixed second virial coefficients were not available for any of the systems, and the approach suggested by Hirschfelder, Curtiss, and Bird (*15*) for polar compounds was adapted to estimate values at the required conditions.

VAPOR PRESSURES

The vapor pressures of the three components have been reported extensively in the literature for the temperature range required, with the exception of acetone. In the case of acetone, some divergence of opinion was apparent as to the variation of vapor pressure with temperature.

A description was needed of the variation in vapor pressure with temperature by equations for use in the digital computer programs compiled for treatment of experimental results and which are described elsewhere (*22*). The type of equation derived by Calingeart and Davis (*7*) from the Antoine equation (*3*) was used. The constants required for the three components are given in Table VII and the vapor pressures are estimated to be better than ±3.0 mm. of Hg of the measured values.

The use of these temperature correlations in calculating activity coefficients and, hence, the constants of the correlating equations, proved to be a successful procedure for correlating isobaric data for the systems of acetone, methanol, and isopropanol.

The constants for the binary forms of the correlating equations considered were obtained directly from experimental data and, also, by graphical means. The constants for the Van Laar equation were obtained graphically from plots of $(\log \gamma_1)^{-0.5}$ *vs.* X_1/X_2 and $(\log \gamma_2)^{-0.5}$ *vs.* X_2/X_1. The constants for the binary Margules equation were obtained graphically from plots of $(\log \gamma_1/X_2^2)$ *vs.* X_2 and $(\log \gamma_2/X_1^2)$ *vs.* X_1. The binary Redlich and Kister equation constants also were obtained by graphical methods using plots of $\log \gamma_1/\gamma_2$ *vs.* X_1.

The mean values of the constants determined by these methods have been used to correlate binary experimental isothermal and isobaric data for the three systems studied. The same binary constants then have been used in the ternary solutions of the correlating equations to correlate the ternary experimental isobaric and isothermal data.

Table V. Ternary Isothermal and Isobaric Data for Acetone-Methanol-Isopropanol

Acetone Mole Fraction X_1 Liquid Phase	Methanol Mole Fraction X_2 Liquid Phase	Acetone Mole Fraction Y_1 Vapor Phase	Methanol Mole Fraction Y_2 Vapor Phase	Temp., ° C.
Isobaric Data at 760.00 Mm. of Hg				
0.0360	0.5460	0.1050	0.6750	69.30
0.0930	0.5230	0.2390	0.5810	66.84
0.1360	0.2980	0.3350	0.3690	68.83
0.0370	0.1120	0.1210	0.1699	76.97
0.8708	0.0761	0.8866	0.0912	56.32
0.5459	0.2693	0.6680	0.2569	58.45
0.3555	0.1917	0.5780	0.2096	63.65
0.0520	0.0287	0.1606	0.0485	77.41
0.1324	0.2635	0.3218	0.3391	69.23
0.0950	0.4453	0.2306	0.5135	68.18
0.0601	0.8993	0.1300	0.8556	63.10
0.1231	0.6965	0.2469	0.6776	63.27
0.3948	0.4841	0.5346	0.4237	58.43
0.2635	0.3920	0.4576	0.3861	62.95
0.3089	0.1895	0.5465	0.2040	64.65
0.0820	0.5602	0.1955	0.6259	66.79
0.3167	0.4201	0.4923	0.4023	61.29
0.3732	0.5910	0.4982	0.4923	57.54
0.4062	0.5355	0.5315	0.4490	57.56
0.4089	0.0351	0.6596	0.0552	64.73
0.4854	0.1379	0.6768	0.1480	61.77
Isothermal Data at 55° C.				Total Pressure, Mm. of Hg
0.8054	0.1760	0.8064	0.1857	746.16
0.7148	0.2306	0.7592	0.2224	730.60
0.5372	0.3447	0.6480	0.3048	695.90
0.0206	0.9580	0.0518	0.9372	521.15
0.0300	0.9070	0.0821	0.8862	519.22
0.0369	0.8940	0.0940	0.8742	530.65
0.0138	0.0616	0.0694	0.1237	266.05
0.0200	0.1071	0.0949	0.1936	278.43
0.0301	0.1163	0.1292	0.2192	300.28
0.4817	0.0761	0.7235	0.0817	579.27
0.4535	0.1450	0.6880	0.1342	585.87
0.4485	0.1723	0.6591	0.1836	595.12
0.3453	0.6239	0.4856	0.5027	685.18
0.3019	0.6707	0.4448	0.5495	672.16
0.2887	0.6475	0.4461	0.5294	657.80
0.0633	0.5681	0.1817	0.6424	464.85
0.0872	0.5249	0.2324	0.5850	467.75
0.0862	0.5420	0.2300	0.5858	472.57
0.0309	0.3907	0.1114	0.5339	376.39
0.0330	0.3646	0.1156	0.5132	371.29
0.0363	0.3395	0.1229	0.4923	366.12
0.2032	0.3236	0.4434	0.3466	502.76
0.2461	0.3081	0.4939	0.3141	528.01
0.3127	0.2807	0.5532	0.2780	559.41
0.8387	0.0970	0.8636	0.1044	720.80
0.8296	0.0677	0.8752	0.0783	705.47
0.7985	0.0707	0.8704	0.0699	693.91

Equation Giving Best Correlating Fit	Binary System	First Constant	Second Constant
Isobaric Data at 760.00 Mm. of Hg			
Redlich and Kister	Acetone-methanol	+0.2779	−0.0080
	Acetone-isopropanol	+0.1977	+0.0065
	Methanol-isopropanol	−0.0573	+0.0040
Isothermal Data at 55° C.			
Redlich and Kister	Acetone-methanol	+0.2935	−0.0152
	Acetone-isopropanol	+0.2871	−0.0117
	Methanol-isopropanol	+0.0332	−0.0108

Table VI. Second Virial Coefficient Data

Compound	Equation for Specified Temp. Range	Temp. Range, ° C.	Lit.
Acetone	$B = -\left[e\,\frac{(-0.009691)}{T} + 10.45\right]$	50–85	(*6, 17, 24*)
Methanol	$B = -100 - 2.148e\,\frac{(2018.0)}{T}$	50–85	(*16, 17, 28*)
Isopropanol	$B = -300 - 0.755e\,\frac{(2483.0)}{T}$	50–85	(*5, 9, 16*)

B = second virial coefficient
e = base of natural logarithms
T = absolute temperature, ° K.

Table VII. Constants for the Vapor Pressure Equations

Component	Constant A	Constant B
Acetone	16.4603	2813.4739
Methanol	18.0958	3377.4522
Isopropanol	19.2578	3942.1312

Table VIII. Root Mean Square Deviations for Acetone-Methanol-Isopropanol

				Range of Deviation					
	Root Mean Square Deviation			Acetone		Methanol		Isopropanol	
Correlating Equation	ΔY_1 Acetone	ΔY_2 Methanol	ΔY_3 Isopropanol	+ *vs.* limit	− *vs.* limit	+ *vs.* limit	− *vs.* limit	+ *vs.* limit	− *vs.* limit
	Present investigation data at 55° C.								
Van Laar by Wohl	0.0061	0.0072	0.0060	+0.0134	−0.0098	+0.0156	−0.0118	+0.0043	−0.0135
Margules by Wohl[a]	0.0070	0.0064	0.0055	+0.0147	−0.0130	+0.0118	−0.0122	+0.0072	−0.0101
Redlich and Kister	0.0058	0.0067	0.0051	+0.0129	−0.0101	+0.0144	−0.0115	+0.0028	−0.0103
	Allen and Pike data (*1*) at 760.00 mm. of Hg								
Van Laar by Wohl	0.0161	0.0178	0.0140	+0.0086	−0.0350	+0.0368	−0.0100	+0.0402	−0.0276
Margules by Wohl[a]	0.0132	0.0167	0.0152	+0.0137	−0.0298	+0.0359	−0.0194	+0.0399	−0.0322
Redlich and Kister	0.0097	0.0146	0.0133	+0.0143	−0.0210	+0.0292	−0.0170	+0.0304	−0.0296
	Present investigation data at 760.00 mm. of Hg								
Van Laar by Wohl	0.0083	0.0080	0.0070	+0.0050	−0.0210	+0.0166	−0.0039	+0.0160	−0.0173
Margules by Wohl[a]	0.0063	0.0074	0.0075	+0.0046	−0.0177	+0.0177	−0.0036	+0.0137	−0.0220
Redlich and Kister	0.0042	0.0050	0.0054	+0.0058	−0.0076	+0.0125	−0.0030	+0.0067	−0.0184

[a] Log γ form.

COMPARISON OF FIT OF TERNARY ISOTHERMAL EQUATIONS WITH ISOBARIC DATA

The closeness of fit and the ability of the equations to predict data have been compared by obtaining the root mean square deviations (R.M.S.D.'s) of the difference between an experimental vapor composition and the predicted vapor composition for that experimental point. The Margules equation (by Wohl) and the Redlich and Kister equation have both been included as in the forms used, ln γ and ln (γ_1/γ_2), respectively; the equation constants are derived by different procedures as previously discussed.

In attempting correlations of ternary data by the ternary solutions of the Margules or the Redlich and Kister equation, the necessity of the ternary constant C must be established or refuted. There is a large amount of evidence (*11*) to suggest that in many instances ternary vapor-liquid equilibrium data can be correlated without a ternary constant.

For the application of the isothermal solutions of the equations to both isothermal and to isobaric data, the values of the constants were calculated as being very close to zero. The mean values for the isobaric data were 0.049 and 0.028 for the ternary Margules and ternary Redlich and Kister equations, respectively. For the isothermal data, the mean values were 0.044 and 0.023 for the ternary Margules and Redlich and Kister equation, respectively. When examined for statistical significance by the t test, the range of values for the constants, in all four cases, was not significantly different from zero.

The experimental determinations in the present investigations were biased towards those areas of the ternary diagram where Severns *et al.* (*26*) have suggested ternary effects are most likely to occur. Thus, the resulting conclusion is that a ternary constant is not required for correlating and predicting data for the system considered, at either of the conditions investigated.

In comparing the use of isothermal equations for isobaric and isothermal correlation, the two sets of isobaric data for the ternary system have been considered separately. Considering the isobaric results in Table VIII, the present investigation has furnished the more accurate data. The reason for the obvious improvement is the more accurate analysis procedure used in the present investigation. Comparing the results for the isothermal and isobaric data from the present investigation the conclusion can be drawn, that by use of the temperature correlations previously described, isobaric data for the system reviewed can be accurately predicted. This, in spite of the system having an over-all boiling temperature range of 27° C.

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Solubility of Gypsum in Sea Water and Sea Water Concentrates at Temperatures from Ambient to 65° C.

LLOYD H. SHAFFER
Research Division, American Machine & Foundry Co., Springdale, Conn.

When strong brines derived from decarbonated sea water are evaporated at temperatures from 35° to 60° C., gypsum, $CaSO_4 \cdot 2H_2O$, forms in the bulk of the liquid. In sea water of normal concentration, the solubility product of this substance is nearly independent of temperature; in the interval 20° to 60° C., the average value is 1.57×10^{-3} (mole)^2/(kg. solvent)^2. In strong brines, six times normal concentration, the solubility product is much greater; it increases from 3.58×10^{-3} (mole)^2/(kg. solvent)^2 at 20° C. to 4.41×10^{-3} (mole)^2/(kg. solvent)^2 at 60° C.

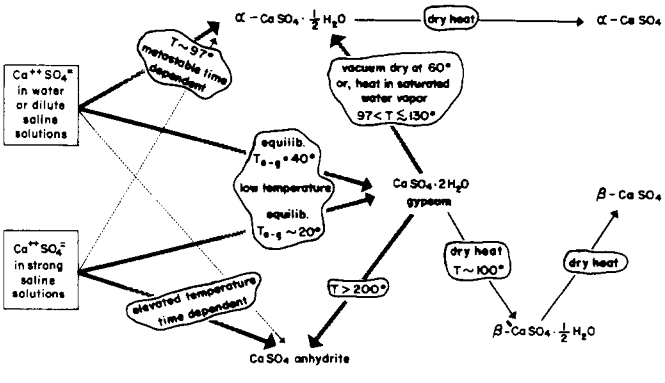
THE FURTHER CONCENTRATION of the brines discharged from conventional evaporator cycles has been studied as part of a continuing program to lower the cost of desalinated water. Tests conducted in 1961 showed that low temperature evaporation would permit the concentration of sea water from a total dissolved solids of 31,000 p.p.m. to over 300,000 p.p.m. without scale formation on the evaporator heat transfer surfaces. These findings have been reported by Fisher and Gilbert (*3*), who also described the triple-effect superconcentrator that was used for further engineering evaluation of the concentration process.

The triple-effect flash evaporator was designed to operate using either sea water or the blowdown from a conventional evaporator as feed. When the evaporator was operated under conditions such that the minimum concentration of the brine circulating in the system was never less than five times sea water, and the maximum temperature was below 65° C., a nonfouling precipitate formed in the brine. This type of operation is achieved through the use of a feed and bleed system in each effect.

The precipitate appeared to be a form of calcium sulfate, and the author thought that the ability to prepare this salt reproducibly would be useful in terms of scale control cycles and by-product recovery schemes. Therefore, the nature of this precipitate has been determined, and the conditions under which it formed have been investigated.

EXISTING DATA

Because of the technological importance of calcium sulfate, a considerable number of papers on this substance have appeared. To put our program in perspective, it is useful to mention briefly some of the more important reviews and sources of data. Posnjak reviewed the material published prior to 1938 (*10*) and, in 1941, Kelly, Southard, and Anderson (*7*) published a comprehensive review dealing with gypsum ($CaSO_4 \cdot 2H_2O$) and its dehydration products. By way of orientation, we have prepared Figure 1, which summarizes the relationships among the various forms of calcium sulfate. Only three—gypsum ($CaSO_4 \cdot 2H_2O$), calcium sulfate hemihydrate (α-hemihydrate), and anhydrite ($CaSO_4$)—can coexist with aqueous systems. The equilibrium temperatures shown for the interconversions between these phases are based on thermodynamic analyses—that is, on the crossing points of the solubility or vapor pressure curves of the various solids; they do not necessarily imply that the transition will occur at the stated temperature. These thermodynamic transition temperatures should be a function of water activity; we found, for example, that gypsum dehydrated to form the hemihy-



all forms convert to anhydrite at temperatures ≳ 200° C., but rapidly only at T ~ 900°

Figure 1. Conversion diagram for various forms of calcium sulfate