Enthalpy-Concentration Charts. Literature Survey and the Two New Systems Isopropyl Alcohol-Water and Acetic Acid-Water

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Enthalpy-concentration diagrams have proved of considerable value in the solution of many problems, particularly those involving mixing, crystallization, and distillation. Unfortunately, however, the lack of certain thermodynamic data together with the tedious nature of the work involved in constructing these charts, has limited their availability to comparatively few systems. Accordingly, a search of the literature was conducted in an effort to locate existing charts. Diagrams for two new systems were constructed.

SURVEY

The results of the search, together with a summary of pertinent information, are presented in Table I. Here 43 references to charts covering 25 different systems are listed. Where one chart is clearly based on another, the original reference is given, unless the later chart includes additional data. Charts for humid air, which can be found in conjunction with psychrometric charts in many places, are omitted.

Charts for most systems listed in the table cover the liquid phase in more or less detail. However, the extent of phase equilibria shown varies considerably from chart to chart. For liquid-vapor equilibrium it ranges from portions of the bubble point line alone to extensive tie line representations involving both bubble point and dew point lines. For solid-liquid equilibrium the variation ranges from incomplete freezing point lines to numerous complete isotherms in the solid-liquid region.

The pressure ranges in the table are given only for those systems having charts showing vapor-liquid equilibrium. For the liquid or solid phase, or equilibrium between the two, the effect of pressure is, of course, small.

Compositions are listed on a weight basis in terms of the first component. Where references to more than one chart are indicated for a particular system, the equilibrium and ranges listed are for the several charts as a group.

ISOPROPYL ALCOHOL-WATER

The general technique for constructing Figure 1, the enthalpy-concentration chart for the system isopropyl alcohol-water, follows the method described by Dodge (*17*). The datum level chosen is that of pure liquids at 32°F. Enthalpies in the liquid region were computed from integral heat of solution data (*15*) at 77°F., heat capacity data for solutions of various concentration (*19*), heat capacity data for pure isopropyl alcohol (*21*, *48*), and the heat capacity for pure water, which was taken as unity. To compute the enthalpy of liquid at any particular concentration and temperature, the enthalpy changes of the pure components from the datum to 77°F. were added to the heat of solution at 77°F. and the enthalpy change of the mixture from 77°F. to the temperature in question. Freezing point data (*30*) made possible placement of the freezing point line. Vapor-liquid equilibrium data at various pressures (*61*) made possible placement of the bubble point lines and, together with subsequent enthalpy calculations for the vapor, the dew point lines and conjugate curves as well.

The enthalpies in the vapor region were obtained by

Table I. Results of Literature Survey

No.	System	References	Phase Equilibria Shown				Range of Variables		
			Solid-liquid	Liquid-vapor	Solid-vapor	Solid-solid	Temp., °F.	Pressure, lb./sq. inch abs.	Composition, wt. %
1[a]	Ammonia-($1/4N_2 + 3/4H_2$)	(6)		x			-58 to 1292	14.2 to 8530	0 to 100
2	Ammonia-water	(*4, 8, 13*)	x	x		x	-149 to 400	0.284 to 300	0 to 100
3	Benzene-toluene	(*3*)		x			50 to 231	14.7	0 to 100
4	Benzene-water	(*5*)		x			54 to 551	2.94 to 735	0 to 100
5	Calcium chloride-water	(*7, 27*)	x	x	x	x	-148 to 1436	2.84 to 28.4	0 to 100
6	Ethyl alcohol-water	(*11, 28, 44, 52*)	x	x			-22 to 302	1.47 to 14.7	0 to 100
7	Ethylene glycol-water	(*14*)		x			60 to 480	4.41	0 to 100
8	Ferrous sulfate-water	(*39*)	x	x	x	x	-40 to 1186	14.7	0 to 100
9	Glycerol-water	(*57*)	x	x		x	-220 to 320	14.7	0 to 100
10	Hydrazine-water	(*57*)	x	x			-130 to 482	14.7	0 to 100
11	Hydrogen chloride-water	(*25, 59*)		x			-121 to 227	14.7	0 to 100
12	Hydrogen fluoride-water	(*58, 60*)		x			32 to 572	14.7	0 to 100
13	Magnesium sulfate-water	(*50*)	x			x	25 to 230	. . .	0 to 50
14	Methanol-water	(*1, 52*)		x			32 to 400	5.80 to 14.7	0 to 100
15	Nitrogen-hydrogen	(*6*)					32 to 1472	4270	0 to 100
16	Nitrogen-oxygen	(*8, 18*)		x			-334 to 80	7.1 to 142	0 to 100
17	Potassium hydroxide-water	(*45*)		x			32 to 932	1.47 to 296	0 to 90
18	*n*-Propyl alcohol-water	(*52*)		x			32 to 212	5.80 to 14.7	0 to 100
19	Silica gel-water	(*29*)					32 to 270	. . .	66.7 to 100
20	Sodium carbonate-water	(*57*)	x	x	x	x	14 to 392	14.7	0 to 100
21	Sodium hydroxide-water	(*2, 12, 16, 22, 56, 57, 62*)	x			x	32 to 900	. . .	0 to 100
22	Sucrose-water	(*9, 54*)	x	x		x	10 to 320	0.284 to 42.6	0 to 100
23	Sulfur trioxide-water	(*10, 23, 53*)	x	x			-4 to 608	14.7	0 to 100
24	Sulfuric acid-water	(*26*)		x			32 to 550	14.7	0 to 100
25	Sulfuric acid-nitric acid-water	(*43*)					32	. . .	0 to 100

[a] Chemical equilibria (ammonia synthesis) presented as well.

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simply summing the enthalpies of the pure components at the given temperature. The very small heat of mixing of the vapor was neglected and calculation based on the well known, generalized, enthalpy change-pressure chart (*24*) showed the effect of pressure on vapor enthalpy negligible at these pressures. Accordingly, the enthalpy of pure isopropyl alcohol vapor was obtained by summing the enthalpy of saturated liquid isopropyl alcohol at the normal boiling point, the normal latent heat of vaporization which is 160 cal. per gram (*34, 41, 49*), and the enthalpy change of pure vapor (*40*) from the normal boiling point to the temperature in question. The enthalpy of pure water vapor was obtained from steam tables (*37*).

ACETIC ACID-WATER

The general method of constructing Figure 2, the enthalpy-concentration chart for the acetic acid-water system, likewise follows the conventional method. The datum level here is the pure components, liquid water and solid acetic acid, at 32°F. By a method analogous to that used for the previous diagram, enthalpies in the liquid region were computed by adding together in the requisite proportions, the enthalpy of pure liquid water at 65°F. relative to 32°F., the enthalpy of pure liquid acetic acid at 65°F. relative to the solid at 32°F., the heat of solution at 65°F. (*36*), and the enthalpy of the solution at the given temperature relative to 65°F. computed from heat capacity data for the solution (*46*). The enthalpy of the pure acetic acid at 65°F. was calculated by summing the enthalpy of pure solid at its melting point of 62°F. relative to solid at 32°F. which was computed from heat capacity data (*31*), the enthalpy of pure liquid at 65°F. relative to liquid at 62°F. which was also computed from heat capacity data (*32*), and the heat of fusion of pure liquid (*33*). Freezing point data (*30*) made possible location of the freezing point line, while enthalpy data for ice (*37*), the heat of fusion for water (*51*), and the corresponding data for acetic acid mentioned above, made possible location of

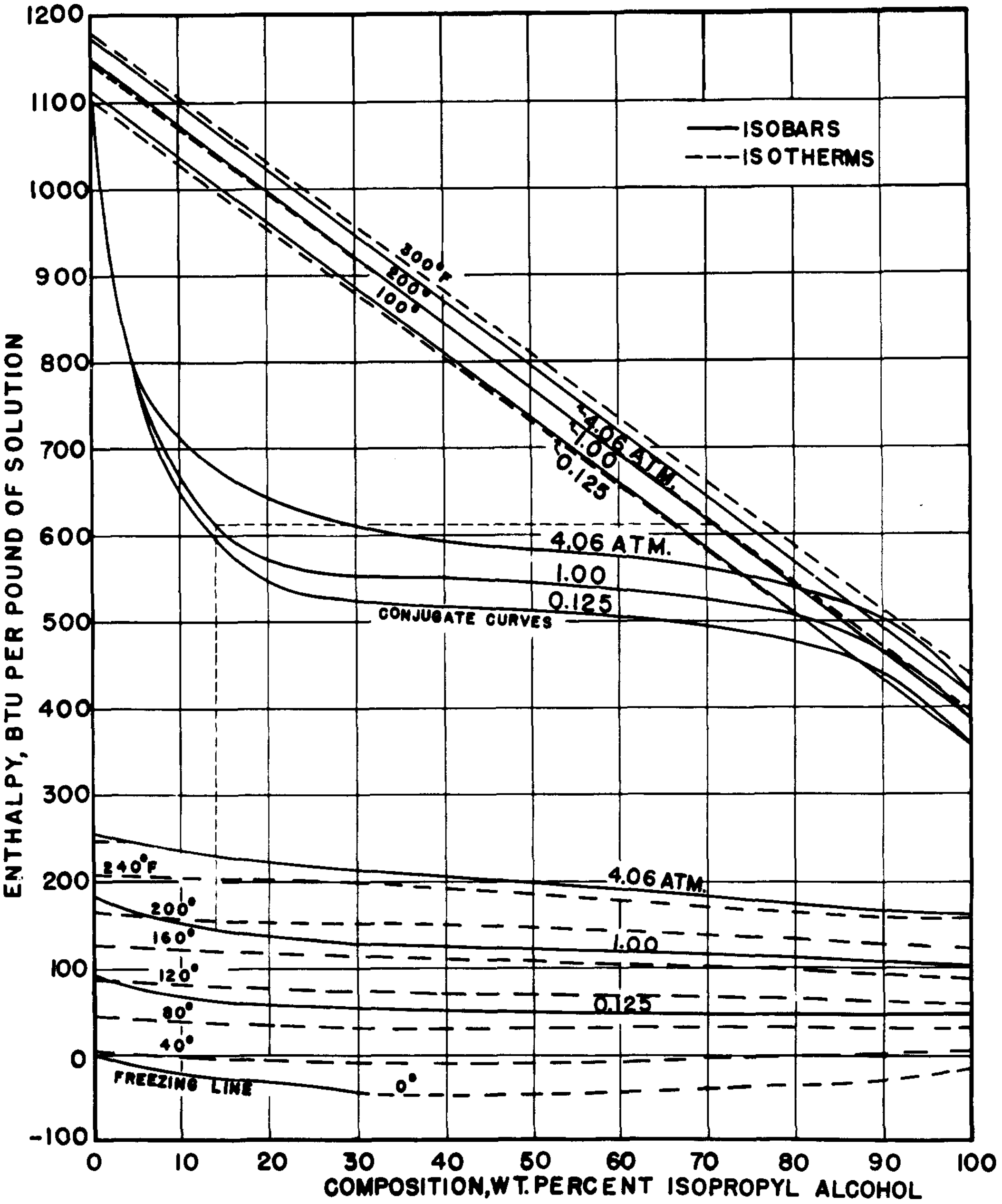

Figure 1. Enthalpy-concentration chart for isopropyl alcohol-water

Application of conjugate curve at 1 atm. illustrated by thin broken line

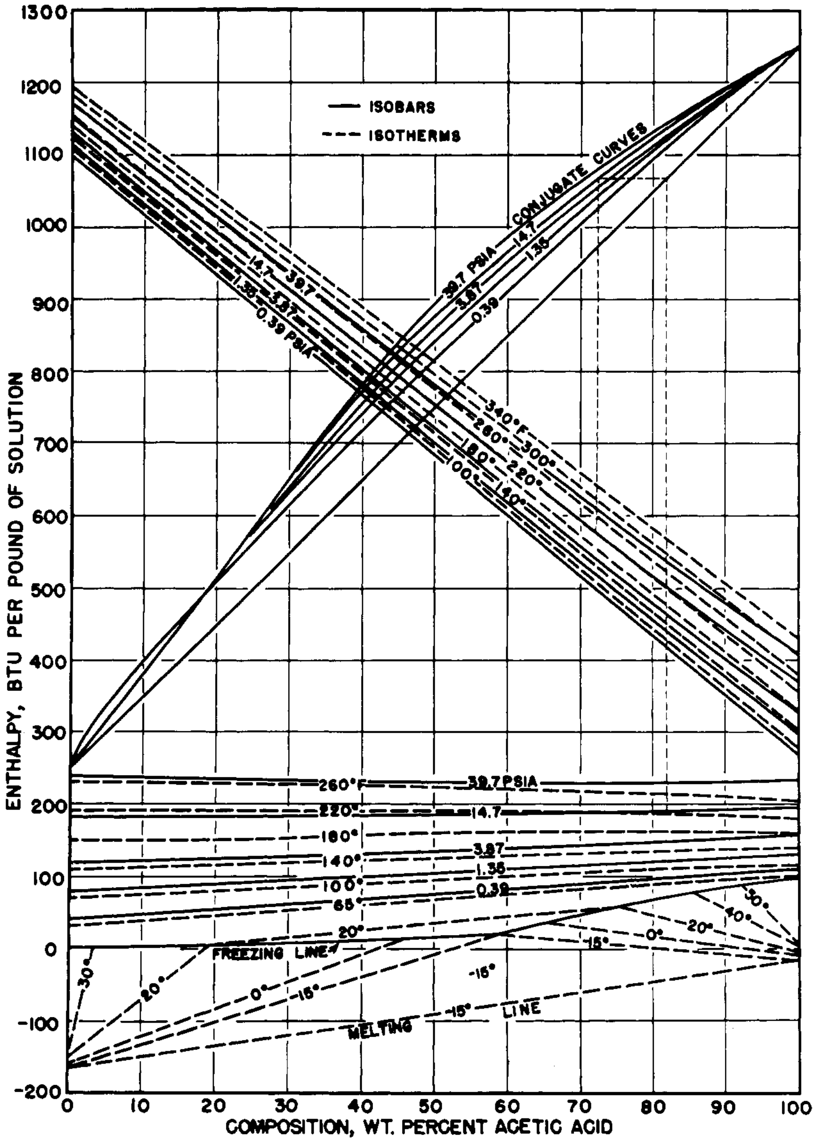

Figure 2. Enthalpy-concentration chart for acetic acid-water

Application of conjugate curve at 14.7 pounds per square inch absolute illustrated by thin broken line

the linear isotherms in the solid-liquid region. No solid hydrates form (*20*, *38*, *55*).

Dew point and bubble point lines, together with conjugate curves, were located by equilibrium data (*47*). As with the first chart, the heat of mixing in the vapor phase was neglected and the enthalpies in the vapor region were computed by summing the enthalpies of the pure vapor components. The enthalpy of pure acetic acid vapor was computed by adding the enthalpy of pure saturated liquid to the heat of vaporization at that temperature (*35*). Calculation showed that any subsequent pressure correction applied to the enthalpy of the acetic acid vapor, because of either dimerization (*42*) or "true" nonideality (*24*), was without significant effect on the enthalpy of the vapor mixture, being less than 1 B.t.u. per pound. As before, enthalpies for steam were taken from steam tables.

ACKNOWLEDGMENT

The authors wish to express their appreciation to William Licht for reviewing the manuscript, to Kaparthi Ramalingam for helping with some of the literature search, and to Roger Keith for inking the figures.

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Received for review February 3, 1956. Accepted June 13, 1956. Division of Industrial and Engineering Chemistry, 130th Meeting ACS, Atlantic City, N.J., September 1956.

Liquid-Liquid Equilibria for Alcohol -Sodium Hydroxide-Water Systems

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Solubility data have been published for sodium hydroxide in aqueous ethyl alcohol (2) and in aqueous isobutyl alcohol (*1*), but no data were available for aqueous isopropyl alcohol (I.P.A.). Information on the solubility of strong caustic soda solutions in isopropyl alcohol and in industrial methylated spirit (I.M.S.) was required for pilot plant neutralization experiments. Industrial methylated spirit is the commercial form of ethyl alcohol available in the United Kingdom.

On refining petroleum, particularly on processing for highly refined white oils by sulfonation, it is necessary to extract oil-soluble sulfonic acids from the sulfonated oil and to neutralize to the corresponding sodium salts. The quality and especially the color of the by-product sodium petroleum sulfonates are influenced by the residence time of the sulfonic acid-oil reaction product, particularly if the equipment is mild steel. For the two systems of processing which may be applied—centrifuge or batch—it is essential that, for the centrifuge process, neutralization and extraction proceed simultaneously, whereas for batch processing it is preferred that the two stages should take place concurrently. For either processing system, it is a distinct advantage if a homogeneous neutralizing-extracting solution is used.

Preliminary experiments indicated that industrial methylated spirit and ethyl alcohol behave differently and it was decided therefore to investigate the systems for industrial methylated spirit and isopropyl alcohol at 25° and 60°C.

MATERIALS

As it was expected that information resulting from this project might be applied to plant scale processing, no attempt was made to purify materials which were of technical quality and had the following properties.

	Specific Gravity at 20°C.	Strength, Weight %
Aqueous caustic soda	1.4590	43.0
I.M.S.	0.8064	94.2
I.P.A.	0.7852	100.0