

- (17) Finke, H.L., Scott, D.W., Gross, M.E., Messerly, J.F., Waddington, Guy, *Ibid.*, **78**, 5469 (1956).
- (18) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
- (19) Hoyer, H., Peperle, H., *Z. Elektrochem.* **62**, 58 (1958).
- (20) Inokuchi, H., Shiba, S., Handa, T., Akamatsu, H., *Bull Chem. Soc. Japan* **25**, 299 (1952).
- (21) Ivin, K.J., Dainton, F.S., *Trans. Faraday Soc.* **43** (1947).
- (22) Jones, A.H., *J. CHEM. ENG. DATA* **5**, 196 (1960).
- (23) Kitaigorodskii, A., "Organic Chemical Crystallography," Consultants Bureau, New York, 1961.
- (24) Klages, F., *Ber.* **82**, 358 (1949).
- (25) Klipping, G., Stranski, I.N., *Z. Anorg. Allgem. Chem.* **297**, 23 (1958).
- (26) "Landolt-Bornstein Physikalischchemische Tabellen," 6th ed., Vol. II, p. 12, Springer, Berlin, 1959.
- (27) London, F.J., *J. Phys. Chem.* **46**, 305 (1942).
- (28) McCullough, J.P., Finke, H.L., Messerly, J.F., Todd, S.S., Kincheloe, T.C., Waddington, Guy, *Ibid.*, **61** 1105 (1957).
- (29) Margrave, J.L., University of Wisconsin, Madison, Wis., private communication, November 1962.
- (30) Meuthen, B., Stackelberg, M. von, *Z. Elektrochem.* **64**, 386 (1960).
- (31) Miller, G.A., *J. CHEM. ENG. DATA* **8**, 69 (1963).
- (32) Myazawa, T., Pitzer, K.S., *J. Am. Chem. Soc.* **80**, 60 (1958).
- (33) Nikolskii, B.P., "Handbuch des Chemikers," Bd. III, Verlag Technik, Berlin, 1959.
- (34) Oliver, G.D., Grisard, J.W., *J. Am. Chem. Soc.* **73**, 1688 (1951).
- (35) Pace, G.E., Aston, J.G., *Ibid.*, **70**, 569 (1948).
- (36) Parks, G.S., Moore, G.E., *J. Chem. Phys.* **17**, 1151 (1959).
- (37) Rathjens, Gwinn, W.D., *J. Am. Chem. Soc.* **75**, 5629 (1953).
- (38) *Ibid.*, p. 5634.
- (39) Rossini, F.D., Pitzer, K.S., Arnett, R.L., Braun, R.M., Pimentel, G.C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Am Petrol. Inst. Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.
- (40) Rowlinson, J.S., Thacker, R., *Trans. Faraday Soc.* **53**, 1 (1957).
- (41) Ruehrwein, R.A., Powell, T.M., *J. Am. Chem. Soc.* **68**, 1063 (1946).
- (42) Sackmann, H., Sauerwald, F., *Z. physik. Chem. (Leipzig)* **A195**, 295 (1950).
- (43) Scheringer, C., Wehrhahn, O.J., Stackelberg, M. von, *Z. Elektrochem.* **64**, 381 (1960).
- (44) Sears, G.W., Hopke, E.R., *J. Am. Chem. Soc.* **71**, 1632 (1949).
- (45) Stevens, B.J., *J. Chem. Soc. (London)* **1953**, p. 2973.
- (46) Thomson, G.W., *J. Am. Chem. Soc.* **76**, 620 (1954).
- (47) Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
- (48) Ungnade, H., McBee, E.T., *Chem. Revs.* **58**, 249 (1958).
- (49) Waghorn, C.G.S., Bradley, R.S., *Proc. Roy. Soc. (London)* **A206**, 65 (1951).
- (50) Witt, R.K., Kemp, J.D., *J. Am. Chem. Soc.* **59**, 273 (1937).
- (51) Wolf, K.L., Weghofer, H., *Z. physik. Chem.* **B39**, 199 (1938).
- (52) Zeise, H., "Thermodynamik," Vol. II, S. Hirzel, Leipzig, 1954.
- (53) Zilberman Granovskaya, A.A., *J. Phys. Chem. U.S.S.R.* **14**, 759 (1940).

RECEIVED for review October 1, 1962. Accepted March 5, 1963. Presented in part at the International Symposium on the Condensation and Evaporation of Solids, Dayton, Ohio, 1962.

Material supplementary to this article has been deposited as Document No. 7609 with the ADI auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$5.00 for photoprints or \$2.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

Measurement of Total Pressures for Determining Liquid-Vapor Equilibrium Relations of the Binary System Isobutyraldehyde-*n*-Butyraldehyde

JÉROME G. WOJTASINSKI¹

Établissements Kuhlmann Laboratoire de Recherches, La Madeleine-lez-Lille (Nord), France

THE HYDROFORMYLATION of propylene (oxo synthesis) leads to the simultaneous formation of the two C₄-aldehydes, *n*-butyraldehyde and isobutyraldehyde. If they are to be chemically converted into other products, these two aldehydes must be completely separated and, for this purpose their liquid-vapor equilibrium diagram is needed.

Bologna and Albonico (2) have published some data relating to this equilibrium, but the thermodynamic

activity coefficients (γ_1 and γ_2) that can be calculated from these data are above unity in the case of one constituent and below unity for the other. This is incompatible with the Duhem-Margules slope law.

The determination of this equilibrium is very difficult, since the use of dynamic apparatus, such as that of Othmer, requires that the products under examination be maintained at boiling point for some considerable time. Aldehydes undergo rapid oxidation and polycondensation reactions under the conditions.

To avoid such reactions, we have resorted to a method based upon the measurement of total pressures. This permits numerous measurements when the required temper-

¹ Present address, Société des Produits Chimiques, Marles-Kuhlmann Chocques (Pas-de-Calais), France.

Isobaric data under atmospheric pressure for the liquid-vapor equilibrium of the binary system *n*-butyraldehyde–isobutyraldehyde have been determined by an indirect calculation, from isothermal data obtained at various temperatures. This method is justified by the tendency of aldehydes to polymerize making it impossible to use the conventional methods involving extended heating. The data obtained have been studied for their thermodynamical consistency which appears to be very satisfactory.

ature has been reached, thus completely avoiding any chemical reactions between the constituent components of the mixture.

Calculation of the partial pressures of the two constituents involved from the total pressure has been effected in accordance with the Boissonas method (1). The values of the activity coefficients have then been deduced from the partial pressures, and they have proved to be in keeping with the laws of thermodynamics.

Finally, the liquid-vapor equilibrium data have been presented in the usual form, using concentration of isobutyraldehyde in the vapor as a function of the concentration of this same constituent in the liquid.

VAPOR PRESSURES OF THE PURE CONSTITUENTS

This calculation requires the knowledge of the exact values of the vapor pressures of the pure constituents. The literature provides few data concerning the vapor pressures of C₄-aldehydes. Only the vapor-pressure curve for *n*-butyraldehyde is known, this being expressed under the form (6):

$$\log p^{\circ} = 7.13708 - \frac{1297.15}{t + 230}$$

No data concerning isobutyraldehyde were found in the literature, so the vapor-pressure curves of these aldehydes were determined experimentally and presented under the usual form:

$$\log p^{\circ} = A - \frac{B}{T} \quad (1)$$

From these experimental values, corrected by the law of least squares, the following equations were obtained:

$$\text{For isobutyraldehyde} \quad \log p^{\circ} = 7.74478 - \frac{1639.22}{T} \quad (2)$$

$$\text{For } n\text{-butyraldehyde} \quad \log p^{\circ} = 7.81818 - \frac{1718.783}{T} \quad (3)$$

CALCULATIONS OF THE PARTIAL PRESSURES FROM THE TOTAL PRESSURE

As it was not possible to use conventional methods, in this work owing to the high reactivity of the aldehydes, a method based upon the measurement of the total pressure was used, the Boissonas method (1).

This method entails the measurement of the total pressure *P* exerted at various temperatures by a mixture of given strength, and the calculation of the partial pressures *p*₁ and *p*₂ from this total pressure, *P*. Once *p*₁ and *p*₂ are known, it is possible to arrive, by a series of mathematical transformations, at the γ_1 and γ_2 activity coefficients (5) and the concentrations *x*₁ and *y*₁ at a given temperature.

If the experiment is repeated with mixtures of various strengths, a series of equilibrium curves is obtained from which the isobaric boiling-point and dew-point curves can be plotted. The basic data that permit the calculation of the partial pressures *p*₁ and *p*₂ are the total pressure *P* and the slopes of the *P* = *f*(*x*) curve at its origins.

By starting with Duhem-Margules equation for partial pressures:

$$x_1 \frac{d \log p_1}{dx_1} + x_2 \frac{d \log p_2}{dx_1} = 0 \quad (4)$$

we arrive by mathematical transformation, at the relationship:

$$\frac{dp_1}{dx_1} = \frac{\frac{dP}{dx_1}}{1 - \frac{x_1 p_2}{x_2 p_1}} \quad (5)$$

From this relation the partial pressures were calculated. In fact, if *P*, *p*₁, and *dP/dx*₁ are known for a small interval of concentration *dx*₁, the *dp*₁/*dx*₁ slope can be calculated for the same interval. This will then give a new value of *p*₁, (*p*₁'), and accordingly *p*₂' = *P* - *p*₁'.

The experimental value of *d'P/d'x*₁ and the new calculated values *p*₁', *p*₂', *x*₁', *x*₂' are then substituted in the formula given above and a new value of *dp/dx*₁ is thus obtained. The calculation may be extended to 760 mm.

In practice, the formula for finite intervals is employed:

$$\Delta p_1 = \frac{\Delta P}{1 - \frac{p_2 x_1}{p_1 x_2}} \quad (6)$$

where

$$\Delta p_1 = \Delta P + p_2^{\circ} \Delta x_1 \text{ for } x_1 = 0 \quad (7)$$

An application of this method for a particular point is illustrated below.

EXPERIMENTAL

Apparatus. The apparatus, represented diagrammatically in Figure 1, comprises a Swietoslawski ebulliometer (7), a trap cooled with dry ice; a 10-liter buffer reservoir, maintained at constant temperature by means of a double jacket in which water is circulated at a fixed temperature; a mercury manometer; and vacuum and compressed-nitrogen supply lines with inlet valves.

The manometer consisted of a U-shaped tube, in 1 meter height. One of the ends of this manometer was connected to the buffer reservoir, the other end was open to the air. The bend of the tube was connected to a large mercury reservoir by a piece of tubing. The U-tube was fixed on a strip of wood graduated in 0.5 mm. The whole assembly could be pivoted on a frame element measuring 1 × 1 meter, provided with graduation lines at 10° intervals.

This system offered the following advantages. It ensured an appreciable displacement of the mercury in one arm of the tube only, and the full length of the manometer could always be used by adapting its angle of slope according to the experimental pressure value.

Purification of Materials. A satisfactory degree of purity was ensured by rectification of the products in a packed column of the laboratory type possessing a high separating power. To avoid any oxidation of the products, a trace amount of hydroquinone (0.2% of the weight of the substance to be distilled) was introduced into the distilling flask.

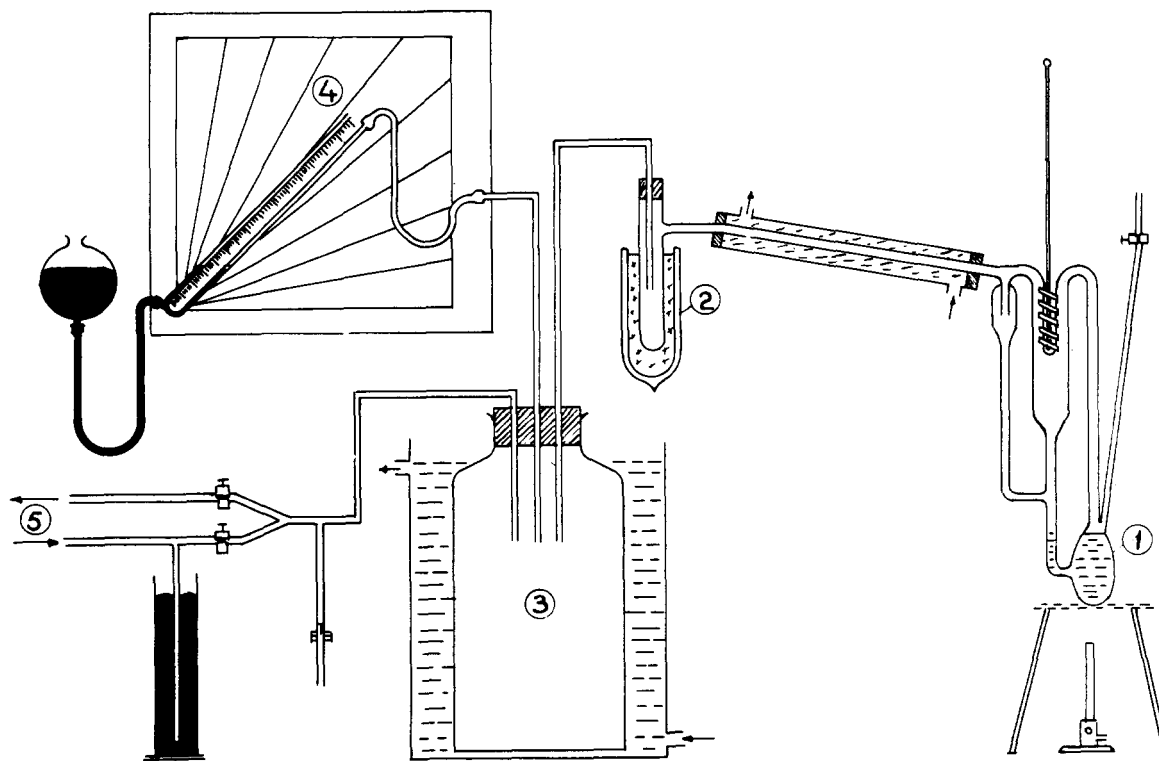


Figure 1. Apparatus for determining liquid-vapor equilibrium by the total pressure method

- (1) Swietoslawski ebulliometer
 (2) Trap
 (3) Buffer reservoir
 (4) Mercury manometer
 (5) Vacuum or compressed air

Analysis for impurities was carried out by the refractometric, densimetric, and chromatographic methods. The refractive indices were determined with a Féry-Vaurabourg refractometer, giving measurements accurate to the fourth decimal place. The specific gravities were determined with a pycnometer. In Table I, the characteristics of the products utilized have been compared with those of the pure products as detailed in the literature.

Procedure. A mixture of known strength was placed in the ebulliometer. A stable pressure was maintained in the apparatus, and the mixture was heated. The temperature at which an equilibrium was reached under the manometer pressure was then noted. A series of $T^0 - P$ data was studied in this way for a mixture of the same composition.

For the reading of the temperature, allowance was made for the correction of the emergent column of mercury by the use of the formula:

$$dt = \eta\alpha(t_a - t_b) \quad (8)$$

RESULTS

The results obtained are listed in Table II and are represented graphically in Figures 2 and 3. Figure 2 shows

the variations in total pressure as a function of temperature for different mixtures. In Figure 3, the isothermal curves have been constructed from these data.

These experimental data enable the partial pressures p_1 and p_2 to be calculated with the aid of Equation 6, following which the activity coefficients can be calculated by the formulas:

$$\gamma_1 = \frac{Py_1}{p_1^0 x_1} = \frac{p_1}{p_1^0 x_1}$$

$$\gamma_2 = \frac{Py_2}{p_2^0 x_2} = \frac{p_2}{p_2^0 x_2}$$

Table III illustrates the calculation of the partial pressures for the 71.5° C. isotherm, corresponding to an isobutyraldehyde concentration of 0.300. For a total pressure of 760 mm., this gives values of p_1 and p_2 equal to 291 and 469 mm., respectively.

In Table IV, the liquid-vapor equilibrium data have been summarized both from the point of view of composition and from that of the activity coefficients. This table indicates that the system isobutyraldehyde-*n*-butyraldehyde is an ideal system since the activity coefficients are very close to

Table I. Purity of Constituents

	n_D^{20}		d_4^{20}		B.P. at 760 Mm. Hg	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
<i>n</i> -Butylaldehyde	1.3845	1.38533(3)	0.8089	0.817(3)	75.12	75.7(3) 74.7(5)
Isobutyraldehyde	1.3729	1.37302(3)	0.7922	0.7938(3) 0.7938(4)	64.01	61.5-63.5(3) 64.0(4)

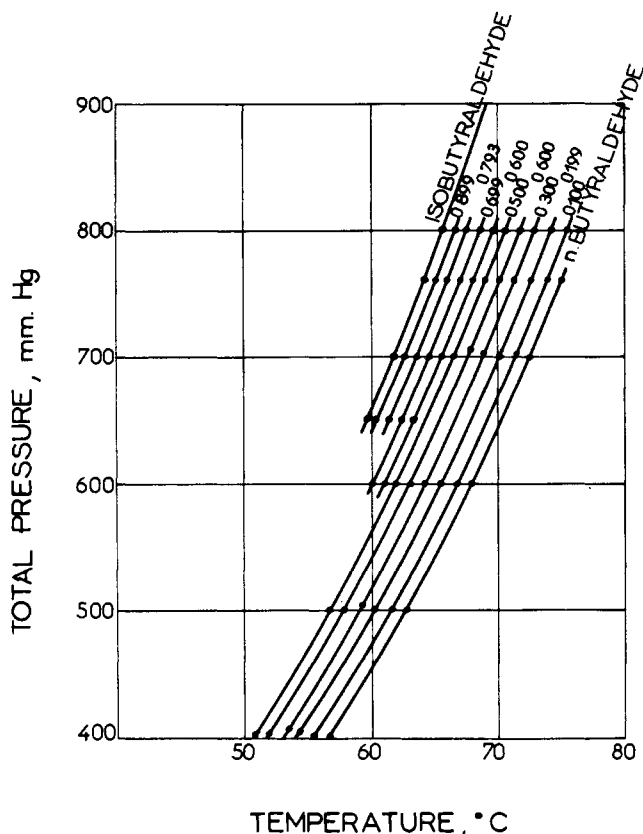


Figure 2. System isobutylaldehyde-*n*-butylaldehyde curves $P = f(t)$

unity for the entire interval represented by concentrations ranging from 0 to 1. The same conclusion could be arrived at if the shape of the isothermal curves alone were taken into consideration. These are in fact perfectly straight lines, which implies that the system obeys Henry's law and Raoult's law throughout the entire interval of concentrations.

The boiling-point and dew-point curves and the liquid-vapor equilibrium curve have been represented in Figures 4 and 5.

CONCLUSION

The study of the binary system isobutylaldehyde-*n*-butylaldehyde shows that this system is an ideal system.

Owing to the fact that these two substances possess very closely-related physical properties and also because of their sensitivity to heat, their investigation entailed the use of a special method which is very different from the conventional methods usually employed. This was based upon the measurement of the total pressures (Boissonnas method). With this method, no analyses are required, and, because of the brief boiling period, degradation of the materials is avoided.

NOMENCLATURE

A, B = Constants of the vapor pressure equation for the pure constituents as a function of temperature, dimensionless

P = Total pressure, mm. of Hg

p_1^0, p_2^0 = Vapor pressure of the pure constituents of the more volatile one and of the less volatile one, mm. of Hg, respectively

p_1, p_2 = Partial pressure of the constituents, mm. of Hg

t = Temperature, °C.

T = Temperature, °K.

t_s = Temperature read on the thermometer, °C.

t_b = Ambient temperature in close proximity to the thermometer, °C.

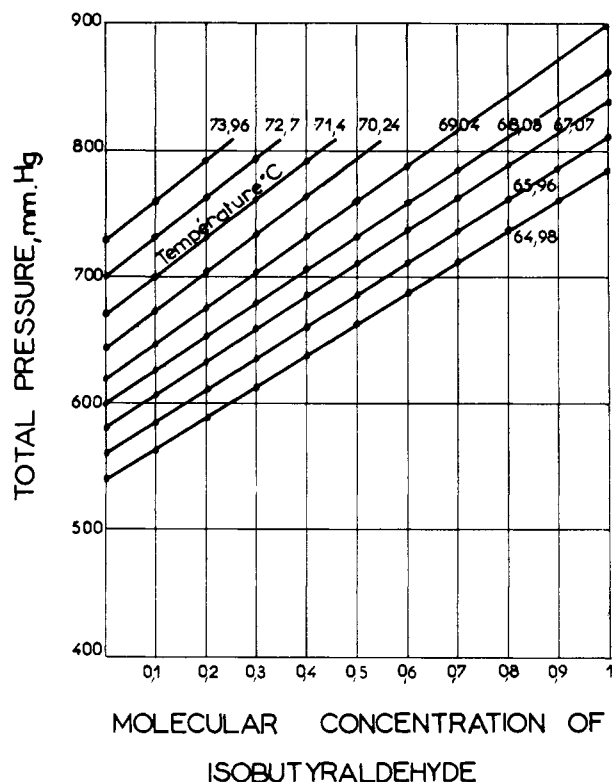


Figure 3. System isobutylaldehyde-*n*-butylaldehyde isothermal curves $P = f(x_1)$

Table II. Experimental Data

P , Mm. Hg	T , °C.	P , Mm. Hg	T , °C.
Isobutylaldehyde		Iso-0.699, Normal-0.301	
651	59.46	600.2	60.03
701	61.68	650.1	62.34
761	64.07	700	64.65
801	65.59	760	67.07
851.1	67.34	800.1	68.58
901.2	69.08	Iso-0.199, Normal-0.801	
950.3	70.90	402.70	54.21
1000.2	72.56	502.70	60.39
1050.2	74.12	600.15	65.63
<i>n</i> -Butylaldehyde		701.20	70.31
400.3	56.51	760	72.69
500.3	62.69	802	74.32
600.5	68.10	Iso-0.300, Normal-0.700	
700	72.71	404.55	53.17
760	75.15	504.55	59.32
Iso-0.100, Normal-0.900		601.70	64.48
401.35	55.37	703.04	69.10
501.90	61.50	760	71.40
603	66.95	803.20	73.08
702.90	71.68	Iso-0.400, Normal-0.600	
760	73.94	403.1	51.83
803	75.63	503.1	57.97
Iso-0.500, Normal-0.500		601	63.26
400.1	50.66	709.20	68.23
500.1	56.79	760	70.24
599.2	62.05	800.60	71.80
700.1	66.67	Iso-0.793, Normal-0.207	
760	69.04	650	61.32
800.15	70.64	700	63.60
Iso-0.600, Normal-0.400		760	65.96
599.7	61.01	800	67.49
649.95	63.35	Iso-0.899, Normal-0.101	
700.1	65.66	650	60.28
760	68.08	700	62.57
800.1	69.59	760	64.95
		800.1	66.44

Table III. Calculation of the Partial Pressures, $x_1 = 0.300$

x_1	P	ΔP	x_1		p_1	p_2	$\frac{p_2 x_1}{p_1 x_2}$	$1 - \frac{p_2 x_1}{p_1 x_2}$	Δp_1
			x_2	p_2					
0	670	15	0	0	670				48.0
0.05	685	15	0.0526	48.5	636.5	0.691	0.309		48.5
0.10	700	15	0.1111	97	603	0.691	0.309		48.5
0.15	715	15	0.1765	145.5	569.5	0.691	0.309		48.5
0.20	730	15	0.2500	194	536	0.691	0.309		48.5
0.25	745	15	0.3333	242.5	502.5	0.691	0.309		48.5
0.30	760		0.4286	291	469				

Table IV. Liquid-Vapor Equilibrium Data for the System Isobutyraldehyde-n-Butyraldehyde

t °C.	p_1^0 Mm. Hg	p_2^0 Mm. Hg	x_1 mole	y_1 mole	Activity Coefficients	
					γ_1	γ_2
73.94	1047.1	731.2	0.100	0.138	1.002	0.996
72.69	1006.7	701.7	0.199	0.264	0.990	0.995
71.40	996.45	672.2	0.300	0.381	1	1
70.24	931.20	646.6	0.400	0.490	1	1
69.04	896	621	0.500	0.589	1	1.005
68.08	868.6	601.1	0.600	0.686	1	0.994
67.07	840.5	580.7	0.699	0.773	1.000	0.990
65.96	810.5	559	0.793	0.846	0.998	1.008
64.95	784	539.8	0.899	0.927	1	1.012

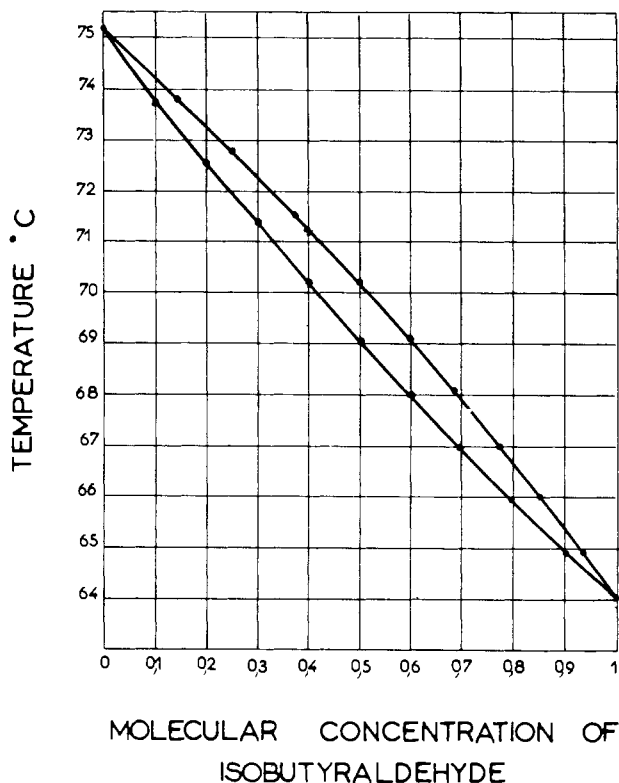


Figure 4. System isobutyraldehyde-n-butyraldehyde boiling-point and dew-point curves

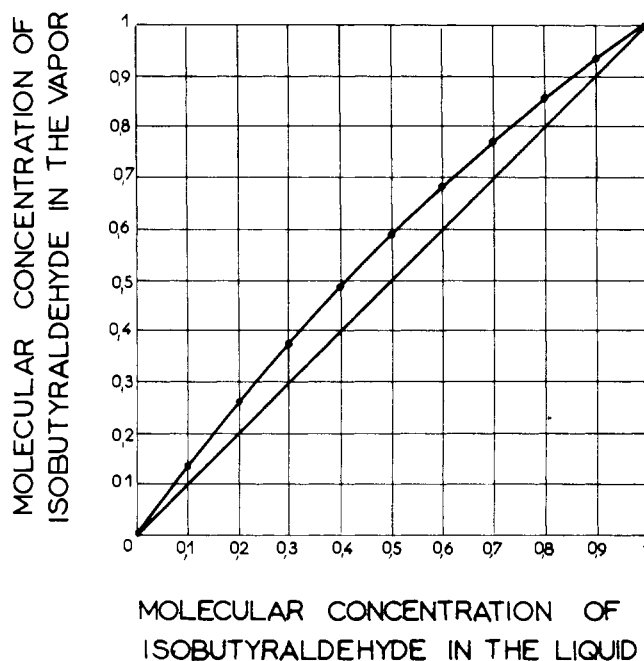


Figure 5. System isobutyraldehyde-n-butyraldehyde liquid-vapor equilibrium curve

- x_1, x_2 = Molar fraction in the liquid of the more volatile constituent and of the less volatile constituent, respectively
- y_1, y_2 = Molar fraction in the vapor of the more volatile constituent and of the less volatile constituent, respectively
- α = Coefficient of apparent expansion of mercury in glass, 1/6300
- η = Height of the emergent column, degrees
- γ = Thermodynamic activity coefficient, dimensionless

LITERATURE CITED

- (1) Boissonnas, C.G., *Helv. Chim. Acta* **22**, 541 (1939).
- (2) Bologna, L., Albonico, F., *Chim. Ind.* **33**, 141-6, (1951).
- (3) Chemical Engineers' Handbook, Perry, J.H., ed., 2nd. ed., p. 280, McGraw-Hill, New York, 1950.
- (4) Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio, 36th ed. p. 987, 1959.
- (5) Paris, A.M., *Les procédés de rectification dans l'Industrie Chimique*, Dunod, Paris, France, 1959.
- (6) Smith, T.E., Bonner, R.F., *Ind. Eng. Chem.* **43**, 1169 (1951).
- (7) Swietoslowski, W., *Roczniki Chem.* **9**, 608 (1929).

RECEIVED for review August 27, 1962. Accepted February 11, 1963.