

# Relative Volatilities of Mixtures of Cyclohexanol and Cyclohexanone in Pressure Range 30–750 mm Hg

Stephen R. Goodwin<sup>1</sup> and David M. T. Newsham<sup>2</sup>

Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

Vapor-liquid equilibrium data are reported for cyclohexanol–cyclohexanone over the pressure range 30–750 mm Hg. Contrary to some previous evidence, this system does not form an azeotrope. A procedure is described for calculating the relative volatilities of this system at low pressures from the values at 750 mm Hg. Good agreement with the experimental results is found.

Two experimental investigations of vapor-liquid equilibria in the system cyclohexanol–cyclohexanone have previously been reported. Cova (2), who presented measurements at 100 mm Hg, found that the system did not form an azeotrope. Engelmann and Bittrich (4) reported measurements at 300, 100, and 30 mm Hg. They found that in ketone-rich mixtures the  $y$ - $x$  curves are concave and that an azeotrope might exist. Their results, however, were not sufficiently precise in this region to be conclusive.

Von Weber (9) discussed the situation. He pointed out that, in industrial distillation columns, the highest purity reached, in the separation of cyclohexanone from cyclohexanol, is 98% and that the composition of the liquid does not change from plate to plate at the top of the column. However, upon examination of the excess functions of mixing (including experimentally determined enthalpies of mixing), he concluded that the deviations from ideal behavior are too small to allow the formation of an azeotrope. He supported this conclusion by carrying out Rayleigh distillations of mixtures of cyclohexanone and cyclohexanol. The situation was complicated by the fact that cyclohexanone undergoes a condensation reaction in which water is eliminated and the condensation product 1-cyclohexen-(1)-yl-cyclohexanone-(2) is formed. Von Weber suggested that the reaction products form an azeotrope with cyclohexanone and that this is the reason for the observed behavior of industrial columns.

This paper reports new measurements for this system over the pressure range 30–750 mm Hg. We used a modified version of the flow still described by Dawe et al. (3). It was necessary to modify the latter because of foaming in mixtures rich in cyclohexanone, especially at the higher pressures. This is discussed more fully below.

This equilibrium still has the advantage that it has such a short residence time that measurements can be made on thermally sensitive materials without significant chemical reaction taking place.

## Experimental

The cyclohexanone and cyclohexanol were SLR grade (Fisons, Ltd., UK) and were fractionated at 10 mm Hg in a laboratory column packed over a 3-ft length with Fenske helices. The distillates were then dried with a molecular sieve and redistilled with a small Vigreux column operating at 10 mm Hg. The condensation reaction

in cyclohexanone proceeds slowly even at room temperature (9); therefore, the sample was refrigerated until required for the experiments. The only detectable impurity in the samples, as indicated by glc analysis, was water at a concentration of <0.01 wt %. For cyclohexanone this concentration possibly represents the limit beyond which it cannot be further purified at room temperature. This arises because water is one of the products of the condensation reaction, and removal of water presumably drives the reaction further to the right.

The modified equilibrium chamber of the flow still is shown in Figure 1. It differs from the previous version in three major respects. First, the vapor inlet tube is sited at the top of the equilibrium chamber. This eliminates the cold spot that could develop in the previous apparatus. Second, the vacuum jacket is replaced by an external heater giving better control of the thermal losses. This is important for high-boiling systems. Third, the droplet separator is redesigned so that measurements can be made on systems that show a tendency to foam. The experimental procedures using this modified still were the same as those previously described.

The pressure in the still was controlled to within 0.1 mm Hg by use of a mercury manometer with a sloping side arm which incorporated an electrical contact. The latter was coupled to an electronic relay and solenoid valve which could vent the still to a vacuum pump. A similar system is described by Ferry (5).

A preliminary study showed that the refractive indices of the binary system were sufficiently composition dependent for them to be used for composition measurement. However, the refractive indices were very sensitive to small traces of water. For example, a concentration of 0.1 wt % of water in cyclohexanone depresses the refractive index by 0.00012. This is equivalent to a compo-

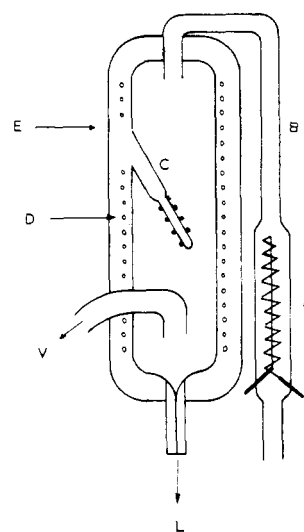


Figure 1. Equilibrium chamber of flow still  
A, boiler; B, Cottrell pump; C, thermometer well; D, heater; E, lagging; V, vapor outlet; L, liquid outlet

<sup>1</sup> Present address, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto 5, Ont., Canada.

<sup>2</sup> To whom correspondence should be addressed.

sition change of 1 wt % in the cyclohexanone–cyclohexanol binary mixture.

Furthermore, the situation is complicated by the redistribution of water between vapor and liquid phases when a sample is passed through the flow still. This technique

**Table I. Boiling Points and Antoine Constants for Cyclohexanone<sup>a</sup>**

<i>P</i> , mm Hg	<i>t</i> , °C	<i>P</i> , mm Hg	<i>t</i> , °C
752.6	154.5	101.6	92.0
750.0	154.4	100.0	91.6
453.3	136.5	49.3	73.6
395.0	131.7	30.0	62.6
394.2	131.5	8.8	38.0
347.4	127.7	5.7	30.6
200.0	110.6	4.2	25.7

<sup>a</sup> Antoine constants: A = 7.4280; B = 1777.7; C = 236.12.

**Table II. Boiling Points and Antoine Constants for Cyclohexanol<sup>a</sup>**

<i>P</i> , mm Hg	<i>t</i> , °C	<i>P</i> , mm Hg	<i>t</i> , °C
750.0	160.1	51.8	91.1
467.9	145.2	30.2	81.0
395.0	140.2	28.5	79.5
386.4	139.7	27.0	78.6
348.5	136.7	11.5	63.8
200.0	121.4	4.25	48.8
193.6	121.0	3.35	46.0
100.1	105.0	3.30	45.5

<sup>a</sup> Antoine constants: A = 7.0385; B = 1318.5; C = 156.60.

**Table III. Vapor-Liquid Equilibrium Data for Cyclohexanol(1)–Cyclohexanone(2)**

<i>P</i> , mm Hg	<i>x</i> <sub>2</sub>	<i>y</i> <sub>2</sub>	<i>t</i> , °C
750	0.116	0.139	159.1
	0.201	0.231	158.2
	0.319	0.358	157.2
	0.455	0.496	156.3
	0.640	0.672	155.3
	0.773	0.792	154.8
	0.841	0.856	154.6
	0.860	0.873	154.6
	0.908	0.918	154.5
	0.908	0.918	154.5
395	0.108	0.147	138.8
	0.228	0.294	137.7
	0.450	0.519	135.4
	0.590	0.654	134.3
	0.831	0.856	132.6
	0.105	0.165	119.6
	0.235	0.337	117.7
	0.438	0.550	115.1
	0.593	0.681	113.4
	0.644	0.722	113.0
100	0.807	0.855	111.6
	0.107	0.185	102.6
	0.247	0.394	99.7
	0.434	0.598	96.3
	0.598	0.713	94.3
	0.740	0.827	92.8
	0.813	0.875	92.2
	0.103	0.217	77.3
	0.232	0.470	73.2
	0.417	0.662	69.1
30	0.600	0.780	66.0
	0.743	0.865	64.4
	0.808	0.903	63.8
	0.808	0.903	63.8
	0.808	0.903	63.8

was therefore abandoned in favor of analysis by gas-liquid chromatography. For this purpose a Perkin-Elmer Model 900 glc was used. The 2-m column was packed with 15% Carbowax 20M on Chromosorb W, 80–100 mesh, and analyses were carried out with the column at 130°C. Peak areas were computed with an Infotronics CRS 204 digital integrator. The system was frequently recalibrated with mixtures of accurately known composition. The precision of the analysis was about ±0.002 in the mole fraction.

## Results

The measured boiling points of the pure components at different pressures are given in Tables I and II, together with the constants of the Antoine equation obtained by the fitting procedure described by Rossini and Pignocco (7).

$$\log_{10} P = A - \frac{B}{C + t} \quad (1)$$

The root-mean-square deviations of the experimental temperatures are 0.14° for cyclohexanone and 0.18°C for cyclohexanol. The boiling points for pressures less than 30 mm Hg were obtained with a batch equilibrium still to be described in a future publication.

The results for cyclohexanol have been compared with the data reported by Novak et al. (6) and selected by Boublik et al. (7). The boiling points calculated from the Antoine constants obtained by Boublik et al. are an average of 0.3°C higher than our values over the pressure range that the two sets of results overlap (50–750 mm Hg). Our results for cyclohexanone are 1.7°C higher and 0.8°C lower than those tabulated by Stull (8) at 5 and 760 mm Hg, and the deviations vary smoothly between these limits.

The results of the vapor-liquid equilibrium experiments are given in Table III and Figure 2. From Figure 2, the system does not form an azeotrope at any pressure below 750 mm Hg. Our results at 100 mm Hg are compared with those of previous workers in Figures 3 and 4. The measured vapor compositions are in close agreement with those of Cova (2) which suggests that the results of Engelmann and Bittrich (4) are almost certainly in error. Figure 4 shows the much higher precision of equilibrium temperatures obtained in this work.

Our results can be subjected to a thermodynamic consistency test based on the following equation:

$$\int_{x_1=0}^{x_1=1} \left[ \ln \gamma_1/\gamma_2 - \frac{H^E}{RT^2} \left( \frac{\partial T}{\partial x_1} \right)_P \right] dx_1 = 0 \quad (2)$$

Figure 5 has been constructed by using extrapolated values of the excess enthalpies reported by von Weber (9) and values for the derivatives  $(\partial T/\partial x_1)_P$  evaluated by graphical differentiation of the boiling-point curve. Because of the rather small values of the ratio  $\ln \gamma_1/\gamma_2$  and of uncertainties in the extrapolated values of the excess enthalpies, as well as unknown errors arising from neglect of vapor-phase imperfection, the experimental points in Figure 5 do not define a unique curve. The actual curve shown in Figure 5 has been constructed to give equal positive and negative areas. Although this gives a reasonable representation of the experimental results, all that can be deduced is that the consistency test is inconclusive. Similar difficulties arise for the results at the other pressures.

**Temperature and composition dependence of relative volatility.** It is sometimes necessary to calculate values of the relative volatility of a binary liquid mixture at pressures lower than those for which experimental data are

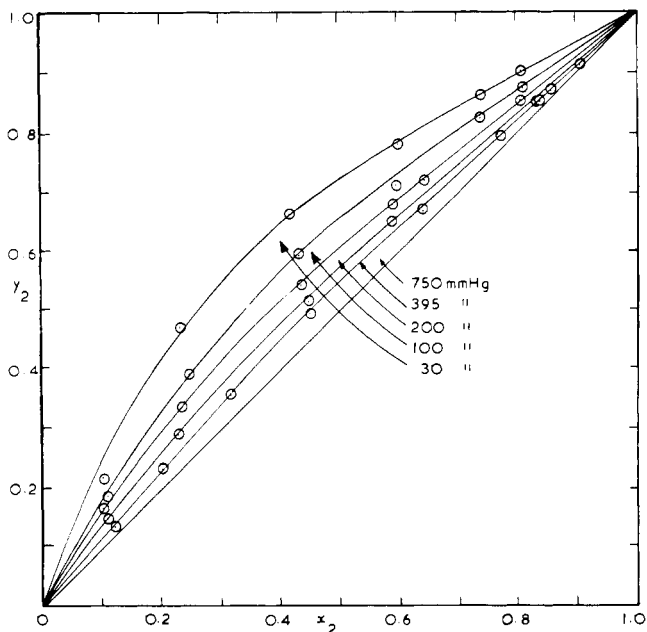


Figure 2. Equilibrium vapor and liquid compositions for cyclohexanol(1)-cyclohexanone(2)

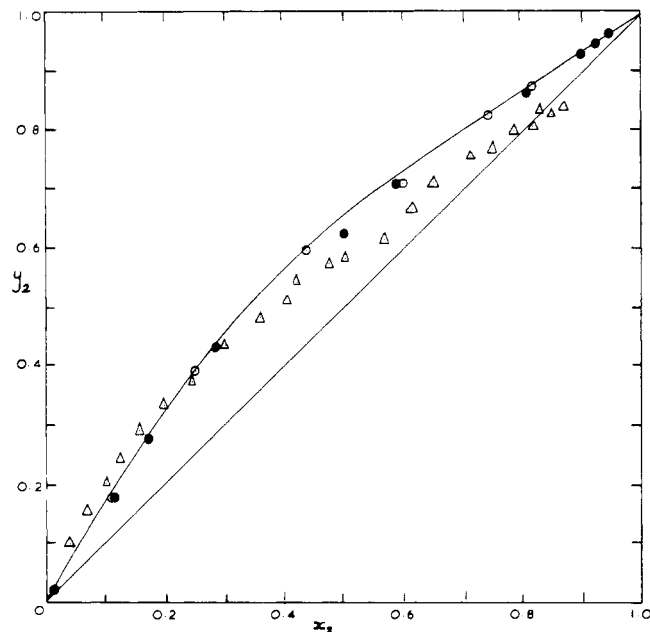


Figure 3. Comparison of vapor-liquid equilibrium data for cyclohexanol(1)-cyclohexanone(2) at 100 mm Hg  
 ○, this work; ●, Cova (2); ▲, Engelmann and Bittrich (4)

available. A thermodynamic extrapolation procedure is outlined below and tested against the data for cyclohexanone-cyclohexanol.

The relative volatility is given by the relation (if vapor-phase imperfection is neglected):

$$\alpha_{ij} = \frac{\gamma_i P_i^\circ}{\gamma_j P_j^\circ} \quad (3)$$

The temperature dependence of  $\gamma_i$  is given by the relation:

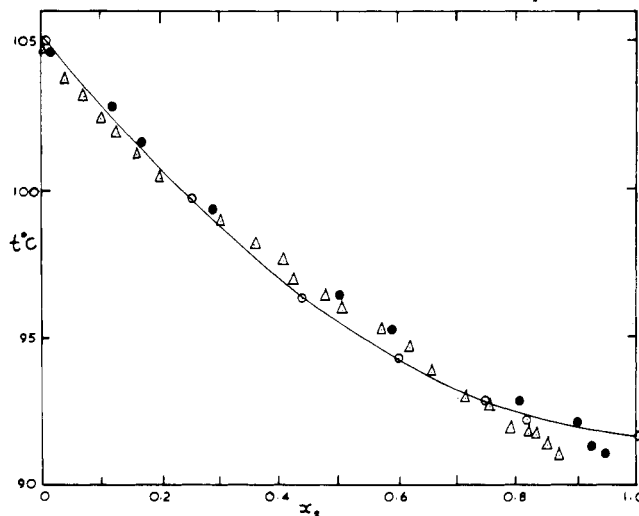


Figure 4. Equilibrium temperatures for cyclohexanol(1)-cyclohexanone(2) at 100 mm Hg  
 ○, this work; ●, Cova (2); ▲, Engelmann and Bittrich (4)

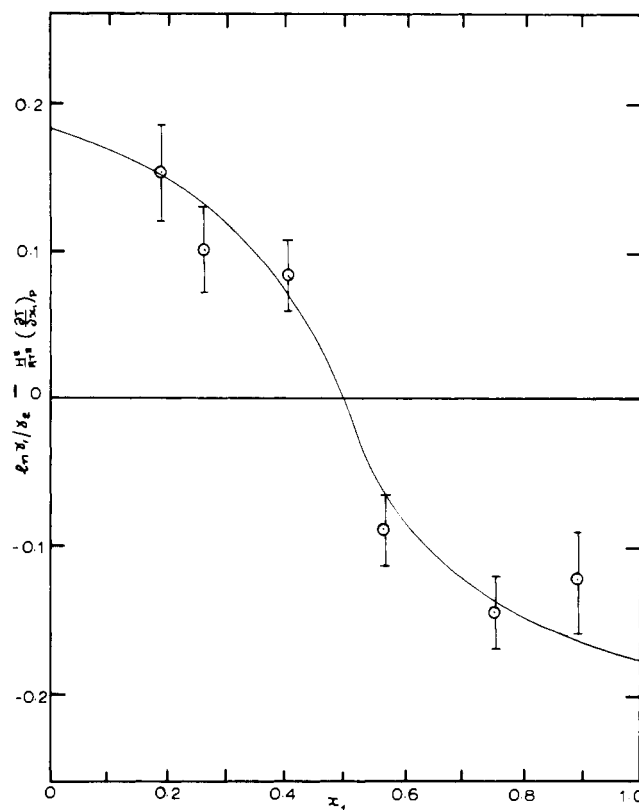


Figure 5. Thermodynamic consistency test for cyclohexanol(1)-cyclohexanone(2) at 100 mm Hg

$$\left( \frac{\partial \ln \gamma_i}{\partial 1/T} \right)_{P, x_i} = \frac{\bar{H}_i - H_i^\circ}{R} \quad (4)$$

The quantity  $(\bar{H}_i - H_i^\circ)$  is, in turn, temperature dependent, and we assume that it is a linear function of temperature. Thus:

$$(\bar{H}_i - H_i^\circ) = (\bar{H}_i - H_i^\circ)_{T_0} + C_i(T - T_0) \quad (5)$$

Substituting Equation 5 into Equation 4 and integrating, we find:

$$R \ln \gamma_i(T) = R \ln \gamma_i(T_0) + (\bar{H}_i - H_i^\circ)_{T_0} \times \left( \frac{1}{T} - \frac{1}{T_0} \right) + C_i \left( 1 - \frac{T_0}{T} + \ln \frac{T_0}{T} \right) \quad (6)$$

If the pure component vapor pressures can be represented by equations of the type:

$$\ln P_i^\circ = A_i + B_i/T \quad (7)$$

then the relative volatility is given by the following relation:

$$\ln \alpha_{ij} = (D_i - D_j) + (E_i - E_j)/T + \frac{(C_i - C_j)}{R} \ln T_0/T \quad (8)$$

where

$$D_i = \ln \gamma_i(T_0) - (\bar{H}_i - H_i^\circ)_{T_0}/RT_0 + C_i/R + A_i$$

and

$$E_i = (\bar{H}_i - H_i^\circ)_{T_0}/R - C_i T_0/R + B_i$$

Thus, the relative volatility may be calculated from a knowledge of the liquid-phase activity coefficients at the reference temperature  $T_0$ , provided that the appropriate vapor pressure and enthalpy data are available.

In Figure 6, values of  $\alpha_{ij}$  calculated from Equation 8 are compared with the experimental data. The agreement is quite satisfactory.

#### Nomenclature

$\left. \begin{matrix} A \\ B \\ C \end{matrix} \right\} = \text{Antoine constants}$

$t = \text{Celsius temperature, } ^\circ\text{C}$

$T = \text{Kelvin temperature, K}$

$P = \text{total pressure, mm Hg}$

$P_i^\circ = \text{pure component vapor pressure, mm Hg}$

$x_i = \text{liquid-phase mole fraction}$

$y_i = \text{vapor-phase mole fraction}$

$\gamma_i = \text{liquid-phase activity coefficient, pure liquid reference state}$

$H^E = \text{excess enthalpy, J mol}^{-1}$

$\alpha_{ij} = \text{relative volatility}$

$\bar{H}_i = \text{partial molar enthalpy, J mol}^{-1}$

$H_i^\circ = \text{pure component enthalpy, J mol}^{-1}$

$C_i = \text{derivative of } (\bar{H}_i - H_i^\circ) \text{ wrt } T, \text{ J K}^{-1} \text{ mol}^{-1}$

$\left. \begin{matrix} A_i \\ B_i \end{matrix} \right\} = \text{vapor-pressure constants}$

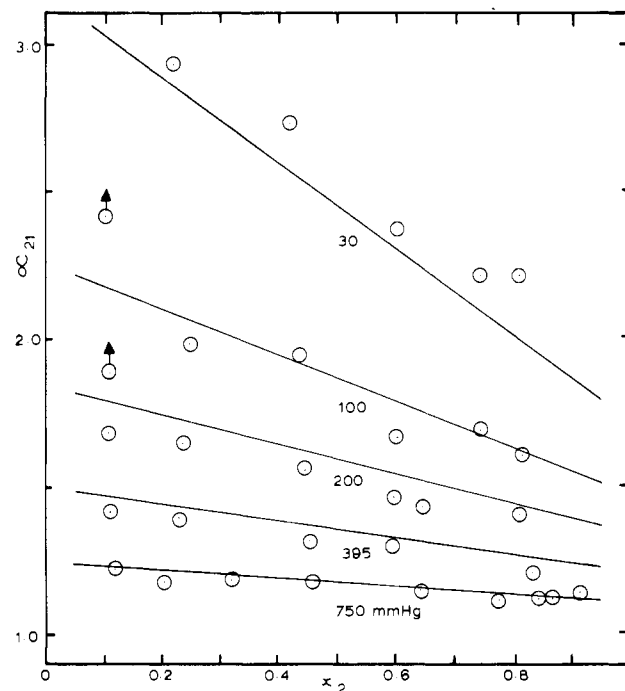


Figure 6. Relative volatilities for cyclohexanol(1)-cyclohexanone(2)

○, experimental; —, calculated, Equation 8

#### Literature Cited

- (1) Boublik, T., Fried, V., Hala, E., "The Vapour Pressures of Pure Substances," Elsevier, Amsterdam, Holland, 1973.
- (2) Cova, D. R., *J. Chem. Eng. Data*, **5**, 282 (1960).
- (3) Dawe, R. A., Newsham, D. M. T., Ng, S. B., *ibid.*, **18**, 44 (1973).
- (4) Engelmann, K., Bittrich, H. J., *J. Prakt. Chem.*, **19**, 106 (1963).
- (5) Ferry, C. W., *Ind. Eng. Chem., Anal. Ed.*, **10**, 647 (1938).
- (6) Novak, J., Matous, J., Pick, J., *Coll. Czech. Chem. Comm.*, **25**, 583 (1960).
- (7) Rossini, F. D., Pignocco, J. M., *J. Res. Nat. Bur. Stand.*, **35**, 219 (1945).
- (8) Stull, D. R., *Ind. Eng. Chem.*, **39**, 517 (1947).
- (9) von Weber, U., *J. Prakt. Chem.*, **312**, 214 (1970).

Received for review February 12, 1974. Accepted June 17, 1974.