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Direct Determination of Enthalpy of Mixing of the Binary Gaseous System N_2–O_2 by Flow Calorimetry

Le B. Ba, Vijay P. S. Nain, Serge C. Kaliaguine, and Rubens S. Ramalho*
Department of Chemical Engineering, Laval University, Quebec, G1K 7P4, Quebec, Canada

A flow calorimeter for measuring enthalpies of mixing of gases was constructed. Enthalpies of mixing for the system N_2–O_2 were measured at four temperatures (10, 25, 45, and 65 °C). For each of the four temperatures, measurements are reported at two pressures: 3.55 and 7.60 MPa (35.0 and 75.0 atm, respectively) for the 10, 45, and 65 °C isotherms, and 3.55 and 6.90 MPa (35.0 and 68.2 atm, respectively) for the 25 °C isotherm. All measurements were made in the gas phase region. The experimental results are compared with predictions using the Redlich–Kwong equation of state, with the mixing rule proposed by Chueh and Prausnitz.

Enthalpy data for pure compounds and mixtures are frequently required for engineering design. Furthermore, enthalpies of mixing (or excess enthalpies) are particularly important on a scientific point of view: since they link directly the enthalpy of a mixture to the enthalpies of its pure components, they are useful to verify predictive methods for thermodynamic properties of mixtures originating from theories based upon assumption of intermolecular forces.

The excess enthalpy for a mixture is defined, at constant temperature and pressure as:

$$H_{T,P}{}^{E} = \left[H_m - \sum_i x_i H_i \right]_{T,P} \tag{1}$$

Although many calorimetric determinations of the enthalpy of mixing of liquids have been made, very few data for gas mixtures are available in the literature. Beenakker et al. (*2, 3, 14, 25*) have studied the systems CH_4–H_2, CH_4–Ar, H_2–N_2, H_2–Ar, Ar–N_2, He–CH_4, and He–Ar. Klein (*12, 13*) investigated the system CH_4–N_2 and Hejmadi et al. (*8, 9*) obtained data for the systems N_2–CO_2, N_2–C_2H_6, and N_2–O_2. Lee and Mather (*16–18*) studied the systems N_2–CO_2 and CH_4–CO_2. Finally, Altunin et al. (*1*) studied the system N_2–CO_2. For the system N_2–O_2 only one experimental point, obtained by Hejmadi (*8*) was available in the literature prior to this investigation, at 6.90 MPa (1001 psia), 25 °C, and 0.522 mol fraction of oxygen. In our investigation, data for the N_2–O_2 system were obtained at four temperatures (10, 25, 45, and 65 °C). For each of the four temperatures, measurements are reported at two pressures, 3.55 and 7.60 MPa (35.0 and 75.0 atm, respectively), for the 10, 45, and 65 °C isotherms, and 3.55 and 6.90 MPa (35.0 and 68.2 atm, respectively) for the 25 °C isotherm, and encompassing a selected range of mole fractions of oxygen in the mixture to permit adequate construction of the entire H^E isotherms from $x = 0$ to $x = 1.0$. All measurements were made in the gas phase region. For more detailed descriptions of equipment and procedures than those presented in this article the reader is referred to ref 15.

Principle of the Experimental Determinations

A flow diagram of the enthalpy of mixing measuring facility is shown in Figure 1. The *central unit* is a *flow calorimeter,* which is specifically designed for direct determination of enthalpies of mixing for *endothermic gaseous systems.* This unit was designed and built at the Instrument Shop, Office of Research Administration of the University of Michigan, Ann Arbor, Mich. In the calorimeter, two gases at the same temperature and pressure are brought together and mixed. For the case of endothermic mixing, a temperature drop occurs. Enough electrical energy is then added to the gases so that the temperature of the effluent gas mixture is brought up to essentially the same value as that of the two incoming gases. Flow rates for each of the pure gas streams are accurately metered, so that the composition of the gas mixture is known. The mixture composition is also periodically checked by chromatographic analysis of the effluent gas mixture. The gas mixture is then discarded to the atmosphere. The enthalpy of mixing is calculated by means of an energy balance, from the knowledge of the gas flow rates and the measurements of the electrical energy input.

The system N_2–O_2, which was the object of this investigation, is actually slightly exothermic. In this case, mixing is thus accompanied by a small temperature rise, which for all our experiments never exceeded 0.1 °C. This adiabatic temperature rise was accurately measured and the enthalpy of mixing calculated by a simple energy balance. In addition to the significant practical importance of precise enthalpy values for the mixture N_2–O_2, the choice of this system, for which the values of the excess enthalpies are very small, was made to demonstrate the high precision which can be obtained with our calorimetric facility.

Our future research program envisions a systematic study of endothermic mixtures, and this is why the calorimeter is specifically designed for this type of system. The excess enthalpies for these endothermic mixtures are two orders of magnitude higher than those measured in the present work.

A description of the equipment and experimental procedure is given in the following sections.

Calorimeter. The calorimeter unit is identical, except for minor design details, with that described by Hejmadi et al., and detailed drawings and description are available in ref 8 and 9. The two gases are mixed and then passed over an electrical resistance coil in the innermost of a series of concentric cylindrical shells which provide both mixing and a heat shield. The gas mixture leaving the outermost shell passes through a helical tube, which conveys it to a thermocouple well. A gold-plated heat shield surrounds the helical coil. The entire unit is enclosed within a jacketed and evacuated space. A vacuum pump (Cenco-Hyvac 7, 1725 rpm, ⅓ hp), indicated as item 19 in Figure 1, is utilized

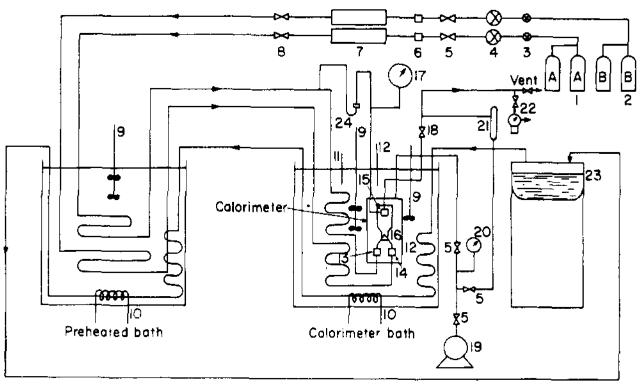

Figure 1. Flow diagram for the experimental apparatus: 1, gas A cylinders; 2, gas B cylinders; 3, pressure regulator; 4, two-stage high pressure regulator; 5, valves for flow adjustment; 6, micron filter; 7, Setaram U-70 mass flowmeter; 8, two way straight valve; 9, stirrer; 10, heater; 11, thermometer; 12, quartz thermometer; 13, pressure tap and thermopile (gas A); 14, pressure tap and thermopile (gas B); 15, pressure tap and thermopile (mixture A + B); 16, gas mixing chamber; 17, gauge (outlet pressure); 18, pressure reducing value; 19, vacuum pump; 20, vacuum gauge; 21, sample tank; 22, wet test meter; 23, Haake KT-64 circulator; 24, Meriam differential manometer.

for this service. A silver-plated copper radiation shield is inserted between the mixing assembly and the vacuum jacket.

Primary Measurements. The primary measurements are temperatures, pressures, flow rates, and electrical power input. The latter was not performed for the case of the N_2–O_2 system for the reason discussed previously.

Temperatures. The *temperature of the calorimeter bath* is measured by a quartz thermometer (item 12 in Figure 1). This is a Model 2801 Dymec, manufactured by Hewlett-Packard, with a 0.02 °C absolute accuracy and calibrated by techniques recommended by NBS. The bath temperature is double checked by an NBS calibrated mercury-in-glass thermometer, with an uncertainty of ±0.03 °C (item 11 in Figure 1). The *calorimeter bath temperature control* is performed by a Bayley precision temperature controller, Model 124, with control range within ±0.001 °C. A 100-W heater (item 10 in Figure 1) operates in conjunction with the temperature controller. In addition a continuous heating system (300 W), connected to a Fisher transistor relay, Model 23, is also utilized to provide heat input to the calorimeter bath. Heat removal from the calorimeter bath is obtained by Haake-Kryothermat KT-64 (item 23 in Figure 1), which is a laboratory circulator containing a built-in cooling compressor and also a continuously variable heating capacity. The circulating fluid is either ethyl alcohol (for temperatures lower than 45 °C) or a silicone fluid (for temperatures above 45 °C). This circulating fluid system is also utilized in the adjustment of temperature of the preheater bath, as indicated in Figure 1. The calorimeter bath is insulated with a 20 cm thick layer of styrofoam, and is filled with a silicone fluid.

The *temperature difference between the entering nitrogen and oxygen gases,* which ideally should be nil, is measured by duplicate six-junction copper-to-constantan thermopiles, connected between wells 13 and 14 in Figure 1. For all reported measurements, the two inlet gas temperatures had to coincide within the accuracy of these measurements, i.e., ±0.002 °C.

The *temperature difference between the entering nitrogen stream* (gas A in Figure 1) *and the effluent gas mixture* is monitored by similar six-junction copper-to-constantan thermopiles, connected between wells 14 and 15 in Figure 1. A Leeds and Northrup null potentiometer (Model 7555, Type K-5) is utilized to measure the output voltage for the two thermopiles described above.

Pressures. Pressure taps are provided at the respective entrances of the pure gases to the calorimeter, i.e., at wells 13 and 14. A pressure tap is likewise provided for the effluent gas mixture, at the well 15. Pressure gauges (Seegers Instruments, with subdivisions of 5 psig) are connected to these pressure taps. The pressures are measured by a dead-weight pressure gauge tester (Budenberg Gauge Co. Ltd, Type 280D), with certificate by the British National Physics Laboratory. The accuracy of the tester is better than ±0.03% of the pressure being measured. The Seegers gauges were only utilized to provide a rapid visual inspection of the order of magnitude of the pressures at any time during the operation. They were calibrated frequently against the dead-weight pressure tester. All pressure values reported in this article were determined by the dead-weight tester. Since the Seegers gauges, as well as the dead-weight tester, are relative instruments, a high precision mercury-in-glass barometer (Hass Instrument Co, Model MS3-V31-11, precision: ±0.34 Pa = ±0.0001 in Hg) was used to read the atmospheric pressure at the time of each measurement.

The *pressure difference between the two entering gases* (taps at wells 13 and 14) is measured by a differential manometer (Meriam Instrument Co., Model 30FA-350PM, with dibutyl phthalate manometric fluid). The differential height is read by a cathetometer. This measurement has the purpose of verifying the uniformity of the entrance pressures for the two gases.

The pressure differences between the influent nitrogen gas (A) and the exit mixture are also measured by the same Meriam manometer (taps at wells 13 and 15). Similarly, *pressure differences between the influent oxygen* (B) *and the exit mixture* are also measured (taps at wells 14 and 15). These last two measurements have the purpose to determine the pressure drop across the calorimeter.

The differential pressures indicated by the Meriam manometer were in general beyond the limit of detection of the human eye, i.e., nil for all practical purposes. Occasionally, it was possible to detect a differential reading, but never greater than 0.05 psi (3.4×10^{-4} MPa).

Flow Rates. The flow rates for the pure gas streams are measured by the two precision mass flowmeters (items 7 in Figure 1). These are manufactured by SETARAM (Lyon, France), Model U-70, and have a precision better than 1%. The operating range of the SETARAM flowmeters is of 0–2000 L h^{-1} at STP (STP defined at 1 atm and 20 °C). This corresponds to 0–0.023 mol s^{-1}. Our base value for the total flow rate (i.e., the combined flow rate for the two-component streams) was of the order of 0.005 mol s^{-1}. Evidently, the individual component flow rates depend upon the composition of the desired mixture, varying from 0 to 0.005 mol s^{-1}, in order to cover the whole composition range. They are, therefore, well below the maximum operating range of the SETARAM flowmeters. The principle of the flow measurement consists in dissipating power into the gas by means of two symmetrical electrical coils placed outside the tubing. In the absence of flow this power dissipation produces a parabolic distribution of temperature along the tube. When there is flow, the temperature distribution curve is distorted, showing cooling on the upstream section and heating on the downstream section. This creates unbalance of a bridge, which is an integral part of the instrument. Voltage ouputs are measured by the Leeds and Northrup null potentiometer (Model 7555, Type K-5) and can be translated in terms of flow rate. Theory and details of the experimental procedure are given in ref 24. The signal output is nearly independent of pressure and temperature. These characteristics are verified by calibration with a wet-test meter (Fisher Scientific Co., Model 63115, accuracy ±0.5%), which is item 22 in Figure 1. The wet-test meter was utilized in checking flow rates through the SETARAM flowmeters at the beginning and at the end of the set of experiments for the N_2–O_2 system. No detectable change in calibration was observed.

The pressure drop across the flow meters is very small (of the order of 4Pa ≈ 0.001 in Hg).

The SETARAM flowmeter is a linear device for our operating range of 0–0.005 mol s^{-1}, independently of temperature and pressure. Only for flow rates above 0.005 mol s^{-1} there is a slight deviation from linearity. Therefore, for the operating range encompassed in this investigation (linear region) the percent precision is nearly independent of the flow rate. The 1% precision value referred to at the beginning of this section applies to the full range of the linear region.

The accuracy of the flowmeter, as indicated in ref 24 is a function of the calibration. It is difficult to estimate the precision and accuracy for the mixture flow rates, but they are better than those values for the chromatographic analysis, for which it is believed that at least a 1% accuracy is a reasonable estimate.

The SETARAM flowmeters are protected from contamination by the microfilters (item 6 in Figure 1). If difficulties occur, such as fluctuations in flow rate measurements or small changes in the pressure of the component streams, there might be an indication of contamination, in which case the microfilters are changed. This is, however, a very rare occurrence. During this entire investigation the microfilters were only changed twice.

From the metered flow rates for each of the pure gases, the composition of the gas mixture can be established. The mixture composition is periodically checked by withdrawing samples into the sample tank (item 21 in Figure 1) and performing chromatographic analysis. The same vacuum pump (item 19 in Figure 1) utilized for evacuation of the calorimeter vacuum jacket is used to evacuate residual gases from sample tank 21. The precision of the chromatographic analysis is of the order of 1%, whereas that for the flow measurements with the SETARAM flowmeters is better than 1%. Chromatographic analysis was performed occasionally only as a qualitative check to detect possible large anomalies. Such anomalies never occurred during our experimental program for the system N_2–O_2.

Power Input. For the case of endothermic systems the power is supplied to the calorimeter by a Kepco, Model SM-325-2A (M) power supply, with regulation to ±0.01%, and is determined by measuring potential drops across standard calibrated resistors, utilizing the Leeds and Northrup K-5 potentiometer.

Operation

Before starting a run, the calorimeter and preheater baths are set at predetermined temperatures. The pure gases ($A = N_2$, $B = O_2$) are contained in two sets of standard gas cylinders, our assembly comprising seven cylinders for each gas. The valves on the gas supply cylinders are then opened. The two pressure regulators, 3 (R-8900, Union Carbide), and the two high pressure regulators, 4 (Hoke, 920 series), permit setting a system pressure within 2% of a predetermined value. In fact, these regulators permit maintenance of a stable system pressure, even though the pressure of the gas in the cylinders drops continuously as the gas is being utilized in the experiments, from a value of about 15.3 MPa (≈ 2200 psig) until a final value of approximately 7.7 MPa (≈1100 psig). At this time the cylinders are cut off from the system by closing the appropriate valves and replaced by a new set of fresh cylinders. Thus for a given reported value of H^E, the pressure fluctuations are negligible.

The Hoke micron filters, 6, are provided as a protection to the flowmeters, 7. Flow rates of the two pure gases are adjusted by means of the valves, 5.

Downstream of each flowmeter there is a two-way valve ($\frac{1}{4}$ in. o.d.), item 8 in Figure 1, which is used to test possible leaks in the flowmeters. If valve 8 is closed and a leak occurs upstream of it, a pressure drop is observed.

It is important that the gas streams do enter the calorimeter at essentially equal temperatures and pressures. For this reason, equal lengths of $\frac{1}{8}$ in. i.d. copper coils (16 meters for the calorimeter bath and 5 meters for the preheater bath) are provided for each gas. The preheater bath is provided with a 100-W heater, identical with the one utilized for heat input to the calorimeter bath.

After passing through the calorimeter, the gas mixture is expanded to atmospheric pressure (pressure reducing valve 18).

The test gases were provided by Canadian Liquid Air Co. The nitrogen has a purity of 99.99%, and contained less than 90 ppm of argon, 20 ppm of oxygen, and 10 ppm of water vapor. The oxygen purity was 99.6%, containing less than 10 ppm of CO + CO_2, 30 ppm of total hydrocarbons, 4000 ppm of argon, 500 ppm of nitrogen and 10 ppm of water vapor. The effect of the slight impurities in nitrogen and oxygen does not affect the H^E values, for which maximum errors are as high as 10%.

Analysis of the Results

Hejmadi et al (*9*) present an expression for the first law of thermodynamics when applied to this flow system, assuming negligible potential energy effects and also negligible rate of heat leak into the calorimeter. From this formulation, the excess molar enthalpy of the gas mixture at the outlet conditions t_o and P_o in the calorimeter is given by:

$$H_o^E = Q/F + x_A(H_{A,1} - H_{A,o}) + x_B(H_{B,2} - H_{B,o}) + \Delta E_k \qquad (2)$$

where:

$$H_{A,1} - H_{A,o} = \int_{P_o}^{P_1} \left(\frac{\partial H}{\partial P}\right)_{T_o} dP + \int_{t_o}^{t_1} C_{P_1,A}\, dt \qquad (3)$$

$$H_{B,2} - H_{B,o} = \int_{P_o}^{P_2} \left(\frac{\partial H}{\partial P}\right)_{T_o} dP + \int_{t_o}^{t_2} C_{P_1,B}\, dt \qquad (4)$$

For our experiments with the system N_2–O_2, we had within the limits of experimental error in the measurements of temperature and pressure that:

$$t_1 = t_2 = t_i \qquad (5)$$

$$P_1 = P_2 = P_i \qquad (6)$$

Furthermore: Since there was no power input to the system, $Q = 0$. It was found that the effect of pressure change from P_i to P_o on the enthalpy of the two pure gases was negligible. Therefore the first of the integrals in eq 3 and 4 do vanish. Since the difference between the outlet and inlet temperatures in this work never exceeded 0.1 °C, it was fully justified to utilize interpolated values for the C_p's (at the arithmetic mean temperature between those of the inlet and exit gases). Therefore the second integrals in eq 3 and 4 can be approximated as $\bar{C}_{P,A}(t_i - t_o)$ and $\bar{C}_{P,B}(t_i - t_o)$, respectively. It was found that the change in molar kinetic energy of the gas stream across the calorimeter was negligible, therefore $\Delta E_k = 0$.

With these simplifications, and letting x stand for the mole fraction of oxygen, eq 2 reduces to:

$$H_o^E = (t_i - t_o)[x\bar{C}_{P,B} + (1 - x)\bar{C}_{P,A}] \qquad (7)$$

Results

The experimental results for the system N_2–O_2 are presented in Table I, and shown graphically in Figures 2–5, at the four nominal temperatures (t_n) and pairs of nominal pressures (P_n). The parabolas in Figures 2–5 were obtained by least-squares fitting of the H^E vs. x data. Nominal temperatures, t_n, correspond to calorimeter bath temperatures and nominal pressures, P_n, correspond to the outlet pressures of the gas mixtures, which are reproducible within a maximum deviation of $\pm 3 \times 10^{-2}$ MPa. The reason for selecting the pressure of 6.90 MPa (68.2 atm) for the 25 °C isotherm was to afford a comparison with the only previously available literature value for the N_2–O_2 system, namely, that of Hejmadi (*8*), mentioned at the introductory section of this article. Hejmadi reports a value of $H_o^E = -3.72$ J g-mol^{-1}. By interpolation of our values for a mole fraction of 0.522, a value of $H_o^E = -3.02$ J g-mol^{-1} is obtained, which represents a deviation of 18.8% with respect to Hejmadi's value. The maximum error in our results, as well as in Hejmadi's is estimated at 10%,

Table I. Enthalpies of Mixing for System N_2–O_2

$\Delta t = t_o - t_i$ (°C)	P_o, MPa	x, mole fraction of O_2	$-H_o^E$, J g-mol^{-1} (exptl)	$-H_o^E$ J g-mol^{-1} (calcd from Redlich–Kwong eq)	Absolute deviation between calcd and exptl values of H_o^E, %
Nominal conditions: t_n = 10 °C; P_n = 3.55 MPa (35 atm)					
0.0338	3.55	0.201	1.05	1.28	21.9
0.0483	3.54	0.352	1.52	1.82	19.7
0.0490	3.55	0.401	1.54	1.92	24.7
0.0541	3.55	0.509	1.70	2.00	17.7
0.0376	3.54	0.754	1.19	1.51	26.9
					Av deviation: 22.2%
Nominal conditions: t_n = 10 °C; P_n = 7.60 MPa (75 atm)					
0.0567	7.59	0.205	1.95	1.97	1.0
0.0810	7.60	0.351	2.91	2.84	2.4
0.0851	7.60	0.402	3.09	3.01	2.6
0.0800	7.60	0.502	2.98	3.16	6.0
0.0770	7.60	0.605	2.93	3.04	3.8
0.0615	7.60	0.751	2.35	2.45	4.3
					Av deviation: 3.4%
Nominal conditions: t_n = 25 °C; P_n = 3.55 MPa (35 atm)					
0.0520	3.55	0.282	1.60	1.58	1.3
0.0581	3.56	0.519	1.81	1.94	7.2
0.0556	3.54	0.565	1.72	1.91	11.1
0.0459	3.56	0.671	1.44	1.73	20.1
					Av deviation: 9.9%
Nominal conditions: t_n = 25 °C; P_n = 6.90 MPa (68.2 atm)					
0.0829	6.93	0.350	2.91	2.76	5.2
0.0853	6.93	0.503	3.02	3.06	1.3
0.0821	6.92	0.581	2.98	3.00	0.7
0.0811	6.91	0.661	2.91	2.79	4.1
0.0485	6.90	0.805	1.88	1.98	5.3
					Av deviation: 3.3%
Nominal conditions: t_n = 45 °C; P_n = 3.55 MPa (35 atm)					
0.0534	3.55	0.346	1.65	1.60	3.0
0.0577	3.54	0.399	1.77	1.70	4.0
0.0592	3.55	0.477	1.84	1.77	3.8
0.0546	3.55	0.605	1.67	1.69	1.2
0.0405	3.54	0.775	1.26	1.24	1.6
					Av deviation: 2.7%
Nominal conditions: t_n = 45 °C; P_n = 7.60 MPa (75 atm)					
0.0876	7.61	0.352	2.84	2.73	3.9
0.0965	7.59	0.501	3.02	3.01	0.3
0.0856	7.58	0.608	2.86	2.90	1.4
0.0739	7.59	0.750	2.33	2.33	0.0
					Av deviation: 1.4%
Nominal conditions: t_n = 65 °C; P_n = 3.55 MPa (35 atm)					
0.0307	3.54	0.197	0.93	1.00	7.5
0.0439	3.54	0.391	1.35	1.54	14.1
0.0515	3.54	0.456	1.58	1.60	1.3
0.0509	3.55	0.568	1.56	1.58	1.3
0.0448	3.55	0.648	1.37	1.46	6.6
					Av deviation: 6.2%
Nominal conditions: t_n = 65 °C; P_n = 7.60 MPa (75 atm)					
0.0329	7.61	0.138	1.05	1.30	23.8
0.0828	7.62	0.349	2.65	2.63	0.8
0.0853	7.59	0.525	2.74	2.86	4.4
0.0610	7.59	0.630	2.26	2.71	19.9
0.0576	7.60	0.749	1.86	2.18	17.2
					Av deviation: 13.2%

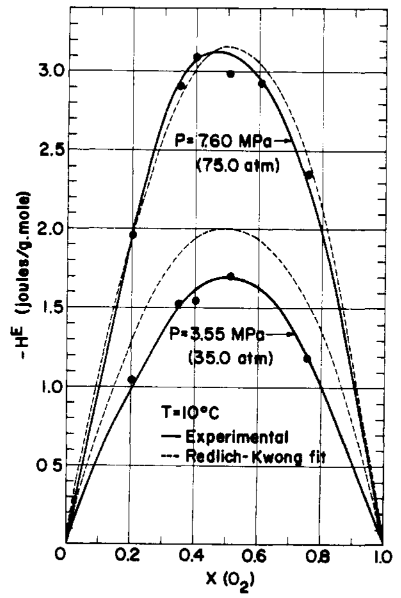

Figure 2. Enthalpy of mixing of N_2–O_2 at 10 °C.

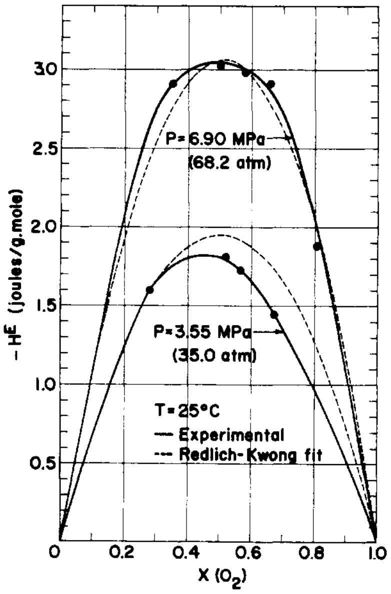

Figure 3. Enthalpy of mixing of N_2–O_2 at 25 °C.

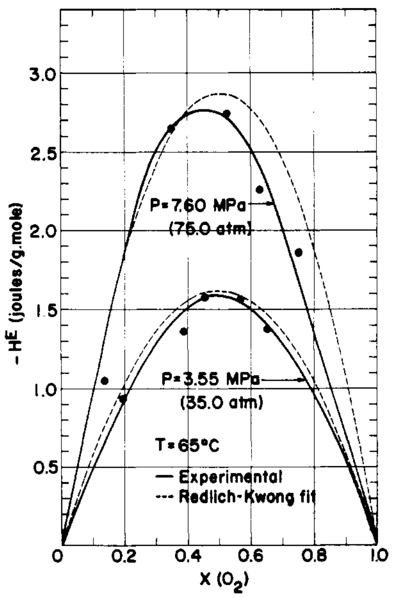

Figure 4. Enthalpy of mixing of N_2–O_2 at 45 °C.

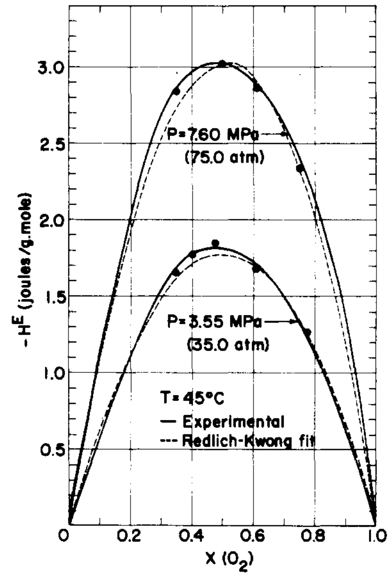

Figure 5. Enthalpy of mixing of N_2–O_2 at 65 °C.

the main contribution to this error being the uncertainty in the temperature measurements. Since only one experimental point was previously available for comparison, the deviation of 18.8% is acceptable.

The enthalpies of mixing presented on the fourth column of Table I were calculated from eq 7, utilizing the heat capacity data from Hilsenrath (*11*), which have an estimated precision of ±1.5%.

A check was performed to assure that the excess enthalpies measured are independent of flow rate, which is a verification of the assumption of adiabaticity of the calorimeter. This testing was based on the technique suggested by Montgomery and De Vries (*20*), which consists in preparing a plot of H^E vs. the inverse of flow rates. This plot, which is available from the authors (*15*), indicated that for variations of flow rate as high as ±40% from a base value (of the order of 5×10^{-3} mol s^{-1}) the deviation on H^E's measured never exceeded 1.5%, which can be considered as a satisfactory test on the adiabatic operation of the flow calorimeter.

The mean uncertainty in the mole fractions is believed to be 0.003. This value as well as other uncertainties reported for this investigation were estimated by a procedure described by Mickley, Sherwood, and Reid (*19*), which involves adding weighted individual accuracies.

Comparison of Experimental Results with Predictions from the Redlich-Kwong Equation of State. The Redlich-Kwong equation of state (*22*) was applied to calculate the excess enthalpies of system N_2–O_2. The modified mixing rule proposed by Chueh and Prausnitz (*7, 21*), in which a characteristic binary constant k_{12} was introduced for the calculation of the parameter a, was utilized for the mixture N_2–O_2. These equations are: Redlich-Kwong equation:

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}V(V + b)} \qquad (8)$$

mixing rules:

$$a = x_1^2 a_{11} + x_2^2 a_{22} + 2x_1 x_2 a_{12} \tag{9}$$

$$b = x_1 b_1 + x_2 b_2 \tag{10}$$

$$a_{11} = \frac{\Omega_{a1} R^2 T_{C1}^{2.5}}{P_{C1}} \tag{11}$$

$$a_{22} = \frac{\Omega_{a2} R^2 T_{C2}^{2.5}}{P_{C2}} \tag{12}$$

$$a_{12} = \frac{(\Omega_{a1} + \Omega_{a2}) R^2 T_{C12}^{2.5}}{2P_{C12}} \tag{13}$$

$$b_1 = \frac{\Omega_{b1} R T_{c1}}{P_{c1}} \tag{14}$$

$$b_1 = \frac{\Omega_{b2} R T_{c2}}{P_{c2}} \tag{15}$$

$$T_{C12} = (T_{C1} T_{C2})^{1/2}(1 - k_{12}) \tag{16}$$

$$P_{C12} = \frac{z_{C12} R T_{C12}}{V_{C12}} \tag{17}$$

$$Z_{C12} = 0.291 - 0.08\left(\frac{\omega_1 + \omega_2}{2}\right) \tag{18}$$

$$V_{C12}^{1/3} = \frac{1}{2}(V_{C1}^{1/3} + V_{C2}^{1/3}) \tag{19}$$

From basic thermodynamic relationships, the following equation relating the enthalpy of a system (pure gas or mixture) portrayed by the Redlich-Kwong equation can be derived:

$$(H - H^*)_o = \frac{b}{V - b} RT - \frac{a}{T^{1/2}(V + b)} - \frac{3}{2}\frac{a}{bT^{1/2}} \ln \frac{V + b}{V} \tag{20}$$

This equation is written for the N_2 and O_2 (as pure gases), and the mixture N_2–O_2. The excess enthalpy H_o^E is then:

$$H_o^E = H_{m,o} - (x_1 H_{1,o} + x_2 H_{2,o}) \tag{21}$$

The values for the acentric factors and the dimensionless constants Ω_a's utilized in our computation were those from Reid and Sherwood (*23*) for oxygen, and from Chueh and Prausnitz (*7*) for nitrogen. The binary constant k_{12} was obtained by a trial-and-error iterative procedure leading to the best possible fit for the excess enthalpy data. We found that a single value of k_{12} equal to 5 X 10^{-4} represents relatively well our entire network of data. The values of all pertinent constants utilized in this computation are presented in Table II.

The fifth and sixth columns in Table I present, respectively, the values of H_o^E calculated from the Redlich-Kwong fit and the absolute percent deviations between calculated and experimental values. Average deviations are indicated at the bottom of the sixth column, for each set of data. It is noticed that the magnitude of the deviations presented in column 6 falls into two categories, one which is about 5% or less and the other averaging 15-20%. The reason for this is as follows: if one utilizes a single value for the binary constant k_{12} over the whole range of pressures and temperatures covered in this investigation it is not possible to represent the data everywhere with the same degree of precision. Data at higher or lower P-T conditions must be "sacrificed" as far as the fitting is concerned, in favor of encompassing reasonably well a wide domain of P-T conditions.

The Benedict-Webb-Rubin equation of state (*4*) yielded erratic results when utilized to portray the excess enthalpy values for the system N_2–O_2. For the application of the BWR equation the oxygen constants set of Hilsenrath (*10*), and the constants for nitrogen from Bloomer et al. (*6*) were utilized. It was also attempted to utilize a modified form of the BWR equation (*5*), but results were still erratic. It is believed that the failure of the BWR equation in portraying our data is mainly due to the incompatibility between the constants for the pure nitrogen and oxygen which were utilized.

Table II. Parameters Pertinent to Computations from Redlich-Kwong Equation

	N_2	O_2
Ω_a, dimensionless	0.4290	0.4278
Ω_b, dimensionless	0.0870	0.0867
T_C, K	126.2	154.8
P_C, MPa	3.39	5.08
ω, dimensionless	0.04	0.021
V_C, cm^3 mol^{-1}	90.1	74.4

Glossary

a	constant in Redlich-Kwong equation, Pa $(K)^{1/2}$ cm^6 mol^{-1}
b	constant in Redlich-Kwong equation, cm^3 mol^{-1}
C_P	molar heat capacity at constant pressure, J mol^{-1} K^{-1}
E_k	molar kinetic energy, J mol^{-1}
F	flow rate, mol s^{-1}
H	molar enthalpy, J mol^{-1}
k_{12}	characteristic binary constant, eq 14, dimensionless.
P	absolute pressure, MPa
Q	power input to the calorimeter, W
R	universal gas constant, J mol^{-1} K^{-1}
T	temperature, K
t	temperature, °C
V	molar volume, cm^3 mol^{-1}
x	mol fraction, dimensionless
z	compressibility factor, dimensionless

Greek Letters

Ω_a, Ω_b	constants in eq 11, 12, and 13, dimensionless
ω	acentric factor, dimensionless

Superscripts

E	designates an excess property
•	designates an hypothetical ideal gas state at temperature *T* and zero pressure

Subscripts:

A	pure gas A
B	pure gas B
Ci	critical constant of gas i (i = 1,2)
Cij	pseudo critical constant of binary system ij
i	either inlet conditions or component i
m	mixture
n	nominal
o	outlet conditions
1	either component 1 or inlet conditions of component 1
2	either component 2 or inlet conditions of component 2

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Isobaric Vapor–Liquid Equilibria for Systems with Associating Vapor Phase Propionic Acid–Isopropylbenzene and Propionic Acid–*o*-Xylene Systems

S. C. Jain, O. P. Bagga, and K. S. N. Raju*
Department of Chemical Engineering and Technology, Panjab University, Chandigarh 160014, India

Vapor–liquid equilibria for the systems, propionic acid–isopropylbenzene and propionic acid–*o*-xylene, were obtained at 760 mmHg using a vapor recirculatory type of still. The activity coefficients were obtained by taking into consideration vapor phase association. Nothnagel's correlation based on chemical theory of vapor imperfections was used. The data satisfied the Herington criterion of thermodynamic consistency and were correlated by the Wilson equation.

This work forms part of an investigation concerning the use of organic acids as separating agents for separation of close boiling hydrocarbon mixtures by distillation. Vapor–liquid equilibrium data have been obtained experimentally for the systems propionic acid–isopropylbenzene and propionic acid–*o*-xylene. Both these systems formed minimum boiling azeotropes. The azeotropic conditions for propionic acid–isopropylbenzene and propionic acid–*o*-xylene systems are 139.00 °C, 72.68 mole % propionic acid, and 136.45 °C, 52.00 mole % propionic acid, respectively, whereas the corresponding values reported by Horsley (*4*) are 139.00 °C, 75.08 mole % propionic acid, and 135.4 °C, 51.94 mole % propionic acid, respectively.

Materials

Isopropylbenzene, *o*-xylene, and propionic acid, laboratory grade reagents from British Drug Houses Limited, were dried over anhydrous blue silica gel and further purified by distillation in a glass column described by Sood et al. (*10*). Table I lists the physical properties of the materials.

Procedure

A modified version of the equilibrium still with circulating vapor phase described by Raju et al. (*8*) was used for obtaining the *t*–*x*–*y* data. The temperature measurements were made by Anschutz type thermometers with an accuracy of ±0.05 °C. The pressure in the still was maintained at 760 ± 1 mmHg. The operation of the still was described elsewhere (*10*).

Equilibrium mixtures were analyzed by density and conductometric titration methods. A pycnometer of 4-mL capacity was used for density measurements. N/20 and N/50 sodium hydroxide solutions were used for finding acid-rich and acid-weak equilibrium mixtures, respectively, while carrying out conductometric titrations. The accuracy of both the methods is of the order of ±0.0002 g mL^{-1}.

Results

Figures 1 and 2 and Table II represent the vapor–liquid equilibrium data obtained in this investigation.

Liquid phase activity coefficients were calculated from the experimental data using the equation (*13*)

$$\gamma_i = \frac{\pi y_i}{P_i^0 x_i} Z_i \qquad (1)$$

where

$$Z_i = \exp\left[\frac{(\pi - P_i^0)(B_i - V_i) + \delta_{ij} y_j^2 \pi}{RT}\right] \qquad (2)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (3)$$

The Antoine equation with constants given in literature (*5, 16*) was used for finding the vapor pressures of pure components as this equation closely represented the vapor pressure data given in literature (*11, 16*) over the temperature range involved. Liquid molal volumes were calculated by the surface tension

Table I. Physical Constants of Pure Compounds

Index	Compound	Density at 25 °C	Bp, °C
1	Isopropylbenzene	0.8576	152.40
		0.8575 (*11*)	152.392 (*16*)
2	*o*-Xylene	0.8758	144.45
		0.8759 (*11*)	144.411 (*16*)
3	Propionic acid	0.9880	140.95
		0.9879 (*11*)	140.99 (*14*)