Measured Enthalpy Changes for a Simulated Natural Gas Mixture and Their Prediction Using a Modified BWR Equation

A new method of incorporating binary interaction data into the BWR equation is proposed. It is developed to predict phase equilibria and enthalpies for multicomponent mixtures using interaction data for 18 binaries.

A calorimeter is described, together with experiments made upon it, for a 6-component simulated North Sea Gas mixture at three pressure levels from 18 to 36 bar, and over a temperature range from 373 to 188K. The experimental enthalpy results are claimed to have an accuracy of ± 0.9%. These results are compared with the predictions of the modified BWR equation. The average deviation is 1.1%, the values being negative at about 18 bar and generally positive for the higher pressures tested.

SOTANDER K. SOOD
and GEOFFREY G. HASELDEN

Department of Chemical Engineering
University of Leeds
Leeds LS2 9JT, England

SCOPE

The purpose of this work was to find an accurate method of calculating the enthalpy of natural gas mixtures of the composition range found in North Sea Gas at pressures and temperatures relevant to liquefier design. Because such gases contain about 95% CH_4 the condensation range occupies only a few degrees. Moreover, the pipeline pressure is near the critical, and economic considerations require that enthalpy values shall have an accuracy of better than 1%. These requirements go beyond the capabilities of existing equations of state and therefore dictate the need for some experimental reference points. The authors have attempted to meet this need by introducing a new interaction parameter into the BWR equation. They have also constructed, and obtained test data on, a new low temperature calorimeter.

CONCLUSIONS AND SIGNIFICANCE

The new calorimeter has proved capable of yielding enthalpy results with an accuracy of better than 1%. More than 20 test points have been generated for a 6-component mixture approximating to the composition of North Sea Gas and spanning a pressure range from 18 to 36 bar and a temperature range of 373 to 188K.

The modified BWR equation incorporating repulsion factors R_{ij}, obtained from published binary mixture data, predicts enthalpy values which differ from the smoothed experimental results by an average absolute deviation of 1.1% This deviation is less than that found for either the unmodified BWR equation or for the Johnson and Colver method, and justifies its use for liquefier design calculations.

SELECTION OF THE EQUATION OF STATE

Since liquefier design calculations extend into the critical region of gas mixtures, there is virtue in using a single equation of state capable of handling the whole vapor-liquid phase space. Alternative approaches based on separate equations for the vapor and liquid phases, such as that of Zellner et al. (1970), have high accuracy away from the critical region but become uncertain close to it.

The Redlich-Kwong equation appears to offer an excellent starting point due to its simplicity. Significant modifications of it have been proposed by Wilson (1965) and by Prausnitz and Chueh (1968), the latter introducing a single interaction parameter. Zudkevitch and Joffe (1970), combining the approaches of Wilson and Prausnitz, have used the equation for both phases. However, for liquefier calculations it is also necessary to handle dense liquids at low temperatures and pressures, together with the highly superheated vapor phase in the compressor. The R-K equation, even in its modified form, will not give good accuracy over all these conditions.

It is a virtue of the BWR equation not only that it can represent a wide range of conditions, but also that it allows different terms to become dominant in different parts of phase space. Thus it permits mixing parameters to be introduced selectively so that they influence, for instance, only the liquid phase calculations. The adopted form of the BWR equation was that incorporating C_0 temperature

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Correspondence concerning this paper should be addressed to G. G. Haselden. S. K. Sood is at Petrocarbon Developments Ltd., Sharston Road, Wythenshawe, Manchester M22 4TB, England.

dependence, the form of this dependency being that published by the authors (1970).

For application to mixtures the eight constants are computed from the pure component values according to rules (Benedict et al., 1951) which have the general form:

$$K_m = \left[\sum_i x_i K_i^{1/L} \right]^L \qquad (1)$$

The following values of L are normally used:

$$\begin{aligned} &\text{for } B_0 && L = 1 \\ &\text{for } A_0, C_0, \gamma && L = 2 \qquad (2) \\ &\text{for } b, a, c, \alpha && L = 3 \end{aligned}$$

Having correlated pure component properties accurately by introducing C_0 temperature dependence, it is reasonable to ascribe any shortcomings of the BWR equation for mixtures to shortcomings of the above mixing rules. The obtuseness of some binary mixtures in defying any simple averaging rules, as demonstrated by Barner and Adler (1968), indicates that an accurate prediction method for multicomponent mixtures should incorporate experimentally determined binary interaction parameters.

Stotler and Benedict (1953) achieved a better fit of phase data for the binary system methane-nitrogen by introducing a specific modification to the squared mixing rule for A_0. They justified their selection of this coefficient by showing that their modified mixing rule was independent of pressure and temperature. Pings and Sage (1956) employed interaction parameters for the methane-pentane binary; however, their method is complex and difficult to generalize. Developing the approach of Stotler and Benedict, Orye (1969) defined a binary interaction parameter M_{ij} for use with the A_0 mixing rule, such that

$$A_{0m} = \sum_i x_i^2 A_{0i} + \sum_{\substack{i \\ j \neq i \\ j > i}} \sum_{j} M_{ij} x_i x_j A_{0i}^{1/2} A_{0j}^{1/2} \qquad (3)$$

This equation reduces to the original mixing rule if $M_{ij} = 2$. Orye did not test his method on multicomponent mixtures and, unlike Stotler and Benedict, found M_{ij} to be temperature dependent. He did not describe the derivation of M_{ij} values. The authors have tested various values of M_{ij} in the modified mixing rules for the methane-pentane system (Sage et al., 1942) firstly for A_0, then for C_0. With neither coefficient could a good fit be achieved.

At this stage the form of the BWR equation was reexamined to check which coefficients exerted a large influence in the liquid region while being insignificant in the vapor phase, since specific intermolecular faces are manifestly most important in the dense phase. The coefficients a and α were found to have the required properties.

It was therefore decided to define a new mixing rule appropriate to a and α incorporating a parameter R_{ij}, such that

$$\begin{aligned} a_m = \sum_i x_i^3 a_i &+ \sum_{\substack{i \\ j \neq i \\ j > i}} \sum_{j} 3/2\, R_{ij} (a_i^2 a_j)^{1/3} x_i^2 x_j \\ &+ \sum_{\substack{i \\ j \neq i \\ j > i}} \sum_{j} 3/2\, R_{ij} (a_j^2 a_i)^{1/3} x_j^2 x_i \\ &+ \sum_{\substack{i \\ i \neq j \neq k \\ i < j < k}} \sum_{j} \sum_{k} 3\, R_{ijk} (a_i a_j a_k)^{1/3} x_i x_j x_k \qquad (4) \end{aligned}$$

where $R_{ijk} = (R_{ij} + R_{ik} + R_{jk})/3$ with a similar equation for α.

Since the above equations have most significance in the dense liquid phase, it was considered convenient and appropriate to refer to the new interaction parameter R_{ij} as the "repulsion factor." Values of R_{ij} are determined from phase data for each binary pair and are then combined for use in multicomponent systems. For the sake of consistency, Equation (4) was made analogous with that of Orye (1969) because when $R_{ij} = 2$ it reverts to the original Benedict mixing rule.

In fitting the new equation to binary equilibrium data for the coefficients a and α, the value of R_{ij} is found for which the sum of the absolute values of the differences in phase fugacities of the components is a minimum. Results were obtained as a set of R_{ij} values over the 2-phase pressure-temperature surface. Table 1 gives a typical set of R_{ij} values, these being for methane-n butane mixtures (data from Sage et al., 1940; Wang and McKetta, 1964). It is apparent that R_{ij} may differ substantially from 2.0 and that it is both temperature and pressure dependent. It increases as the temperature decreases and also as the pressure decreases in the range 120 to 20 bar.

Comparing the behavior of the repulsion factor for various binaries, it was evident that its use was particularly valuable for wide-boiling mixtures such as methane-n butane. It successfully corrected the liquid fugacity of the highly supercritical lighter component without altering the fugacities of the heavier component significantly. Figure 1 illustrates the manner in which variation of R_{ij} brings the phase fugacities together for another wide-boiling mixture, nitrogen-ethane. In this case the best value of R_{ij} is much less than 2.0.

In the absence of any theoretical insights into the temperature and pressure dependency of R_{ij}, it was decided to represent it by an empirical equation using reduced properties.

$$R_{ij} = q_1 \, (T/T_{c_{ij}})^{q_2} \, (P/P_{c_{ij}})^{q_3} - q_4 \qquad (5)$$

where $T_{c_{ij}} = (T_{c_i} + T_{c_j})/2$, $P_{c_{ij}} = (P_{c_i} + P_{c_j})/2$.

Values of the constants q_1 to q_4 were found for each

TABLE 1. R_{ij} VALUES FOR METHANE-n BUTANE MIXTURE

T K	P atm	R_{ij}
277.61	27.22	6.89
277.61	54.44	4.52
277.61	81.65	3.88
277.61	115.68	3.27
294.27	20.41	8.27
294.27	40.83	5.36
294.27	68.05	4.36
294.27	102.07	3.71
294.27	129.29	3.20
310.94	20.41	8.14
310.94	40.83	5.17
310.94	68.05	4.18
310.94	102.07	3.57
310.94	129.29	3.18
327.60	40.83	4.96
327.60	102.07	3.30
327.60	125.88	2.83
344.27	27.22	6.00
344.27	40.83	4.78
344.27	68.05	3.80
344.27	122.48	2.44
360.93	27.22	5.18
360.93	68.05	3.49
360.93	112.27	2.22

binary mixture by fitting with an unweighted least squares procedure. q_4 only takes values for those binaries in which some of the R_{ij} values are negative.

Table 2 presents values of the interaction equation parameters for 18 binary systems. Extrapolation of Equation (5) to values above the temperature range or below the pressure range indicated in Table 2 is not recommended. No systematic pattern of behavior of the parameters q_1 to q_4 could be detected.

Using fitted R_{ij} values and C_0 temperature dependence for all components, vapor-liquid equilibria were calculated for two binary, four ternary, and one quinary mixture. A Bubble Point program was used which determined the total pressure and vapor composition for each input temperature and liquid composition. The results are presented in Table 3 for both K-values and the predicted pressure. The latter provides the more effective test since it aggregates the predictions for all components. It is seen that the use of the preferred R_{ij} values reduces the error in P by a substantial factor in every case.

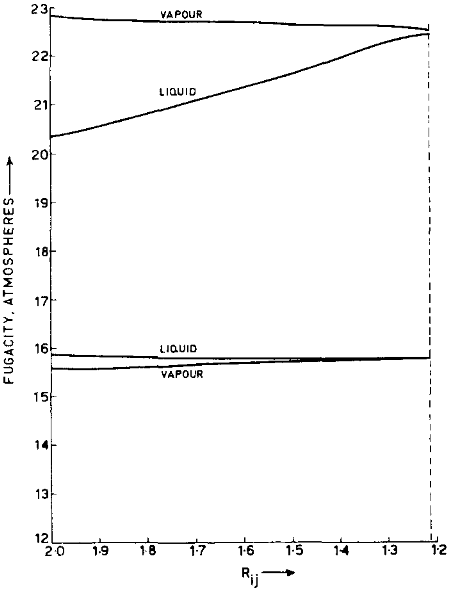

Fig. 1. The influence of R_{ij} values in promoting the convergence of fugacities for the system nitrogen-ethane at 266.49K and 47.6 atm. The upper pair of curves are for nitrogen and the lower ones for ethane. The selected value of R_{ij} was 1.21.

EXPERIMENT

The design of the calorimeter is shown in Figure 2. The inlet tube on the left-hand side contains a coiled electric heater which is thermostatically controlled by reference to the capsule-type platinum resistance thermometer situated immediately below it. The temperature of the inlet gas is measured at entry to the cooling coil by a copper-constantan thermocouple. The cooling coil has a few suspended turns to provide a heat brake, the remaining turns being soft soldered to the outside of the supporting cylinder. This cylinder also serves to conduct heat downwards to the base of the central evaporator. This evaporator contains a central plug running in a screw thread, and the position of the plug determines the level of liquid oxygen within the evaporator. The varying liquid contact area and the tapered form of the stainless steel evaporator wall provides for a cooling range of about 25:1.

Liquid oxygen was used as coolant in preference to nitrogen for three main reasons. It enabled much longer runs to be made with a single supply dewar due to the higher latent heat per unit volume of oxygen. It minimized the chance of solid methane blockage in the cooling coil during a temporary shutdown. It was not subject to impurity accumulation leading to bath temperature change since the likely components (N_2 and A) are both more volatile. The design of the apparatus which conveyed the test gas and coolant in quite distinct flow systems, separated by a vacuum space, eliminated explosion hazards.

The cold test fluid leaving the cooling coil entered a sampling chamber in which its temperature was measured and the separate pockets for vapor and liquid samples became charged. The test fluid left through a vertical capillary tube with a

TABLE 2. BINARY PARAMETERS FOR THE R_{ij} CORRELATING EQUATION
(Data sources given by Sood, 1971)

Binary mixture	Temperature range, K	Pressure range, atm	q_1	q_2	q_3	q_4	Standard mean deviation
Nitrogen-*n* butane	310 to 377	16 to 232	10.20859	-2.829170	-4.828371×10^{-1}	0	2.54×10^{-1}
Methane-*n* butane	177 to 394	6.8 to 125	5.441928	-1.488433	-5.511290×10^{-1}	0	8.61×10^{-2}
Methane-ethane	144 to 283	6.8 to 68	2.419323	3.341869×10^{-1}	4.975753×10^{-2}	0	5.34×10^{-2}
Methane-propane	144 to 344	6.8 to 95	1.936278	-2.045442×10^{-1}	1.343522×10^{-1}	0	2.87×10^{-2}
Methane-*n* pentane	310 to 444	13 to 136	2.422168	1.409425	-1.850206×10^{-1}	0	2.34×10^{-1}
Methane-*n* hexane	310 to 410	34 to 188	2.287123	1.407574	-2.191014×10^{-2}	0	6.08×10^{-2}
Methane-*n* heptane	188 to 444	13 to 204	2.445472	$-8\ 661585 \times 10^{-2}$	-3.196467×10^{-2}	0	3.50×10^{-2}
Ethane-propane	310 to 366	20 to 51	2.041524	-4.514797×10^{-1}	-2.272157×10^{-1}	0	3.06×10^{-2}
Ethane-*n* butane	338 to 394	30 to 55	2.194927	-1.037228	-4.845292×10^{-1}	0	4.36×10^{-2}
Ethane-*n* pentane	277 to 410	6.8 to 61	2.092229	5.431703×10^{-3}	6.562160×10^{-2}	0	3.80×10^{-2}
Propane-*n* pentane	344 to 444	6.8 to 40	2.259954	-6.632475×10^{-1}	2.876382×10^{-1}	0	1.04×10^{-1}
Nitrogen-methane	110 to 172	3.4 to 44	1.560851	2.855034×10^{-1}	-7.290245×10^{-2}	0	6.29×10^{-2}
Nitrogen-ethane	133 to 266	6.8 to 81	1.536531	-7.643742×10^{-1}	2.633450×10^{-2}	0	2.80×10^{-2}
Nitrogen-*n* hexane	310 to 444	17 to 80	2.531406	-9.231286×10^{-1}	-1.332963×10^{-1}	0	1.17×10^{-1}
Methane-hydrogen sulphide	188 to 330	13 to 81	-1.236377×10^{-1}	1.268509×10^{1}	-4.369224	0	1.13
Methane-carbon dioxide	199 to 271	14 to 76	1.680921	-6.119476	2.546102	-1.0000	1.96×10^{-1}
Hydrogen sulphide-carbon dioxide	249 to 355	10 to 80	2.846119	-6.916690	1.408361	-2.0000	1.79×10^{-1}
Hydrogen sulphide-*n* pentane	277 to 444	6.8 to 81	2.224621	5.721122×10^{-1}	2.115108×10^{-1}	0	3.49×10^{-2}

Table 3. Calculated Results Without and With Repulsion Factors

Mixture	No. of data points tested	Avg. abs. % deviation of K for first component		Avg. abs. % deviation in predicted pressure P	
		All $R_{ij} = 2.0$	Optimum R_{ij}	All $R_{ij} = 2.0$	Optimum R_{ij}
Methane-*n* pentane (Sage et al., 1942)	12	1.23	0.89	4.21	0.82
Ethane-*n* pentane (Reamer et al., 1960)	6	0.45	0.36	2.64	1.01
Methane-ethane-propane (Price and Kobayashi, 1959)	16	0.64	0.48	4.28	2.01
Methane-propane-*n* pentane (Dowson et al., 1943)	7	0.93	0.90	3.80	2.14
Nitrogen-methane-*n* butane (Roberts and McKetta, 1962)	8	13.81	9.07	29.34	3.38
n-Butane-methane-carbon dioxide (Wang and McKetta, 1964)	4	14.64	13.64	45.57	6.55
Methane-ethane-propane-*n* butane-*n* pentane (de Priester, 1953)	7	2.44	2.49	9.97	3.09

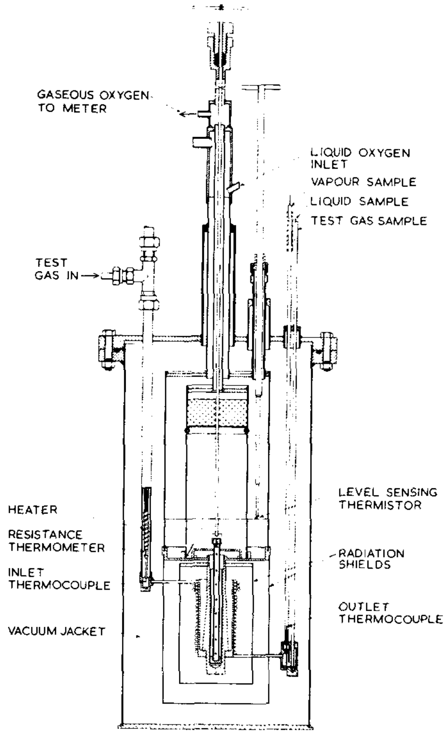

Fig. 2. Diagram of the flow calorimeter. The cooling coil contained a turbulence promoter. The phase separator was designed to isolate vapor and liquid samples but not to achieve a complete separation of the product stream.

45° bevelled end. The termination of this tube automatically set the liquid level in the sampling chamber.

Two radiation shields were installed between the cooling coil and the surrounding vacuum jacket to minimize heat inleak. Also the cooling coil and the sampling chamber were each covered with a few layers of superinsulant.

The completed calorimeter was calibrated for residual heat leak by test runs with gaseous nitrogen over a range of flow rates and temperatures. A series of experiments was then made with a simulated natural gas mixture at three pressure levels. In all cases the inlet temperature was held constant at about 100° C. The results, corrected for heat inleak, were then cross-plotted to check for random errors and finally corrected to an exact inlet temperature of 373.15K; these are presented in Table 4. A fuller account of the experimental procedure and method of evaluation is given by Sood (1971).

The heat inleak was found to be a function of the refrigerant oxygen flow rate, and reached a maximum value of about 600 cal/h when the flow rate was about 300 l/h corresponding to a total heat flux of about 18,000 cal/h. The RMS deviation of the estimated heat leak was 63 cal/h corresponding to a maximum uncertainty of ±0.35% in the computed enthalpy change. For most test runs the heat flux was considerably greater and the error was therefore less.

For the case of a typical natural gas experiment in which the heat flux was 2,500 cal/mole the following sources of uncertainty were estimated:

Measurement	Resultant error, cal/mole
Inlet temperature, ±0.11°C	±1.2
Exit temperature, ±0.10°C	±2.8
Pressure, ±2.0 lb./sq.in.	±2.0
Volume of test gas, ±0.14%	±3.5
Volume of oxygen, ±0.15%	±2.8
Latent heat value for oxygen	±0.5
Heat leak correction	±4.5
Overall mixture analysis, ±1.5%	±5.3
Total	±22.6

The total error is thus seen to represent an uncertainty of ±0.9% in the experimental enthalpy determination.

DISCUSSION OF RESULTS

It did not prove experimentally possible to obtain many results for this type of mixture in the 2-phase region. This was because with more than 95% of methane present in the feed the whole 2-phase region is compressed into approximately 5K. The quality of control, not only of temperature but also of pressure and flow rate, was inadequate for this challenge.

The experimental corrected enthalpy changes are compared in Table 4 with the values predicted by the modified BWR equation using R_{ij} values where available. At pressures of about 18 bar it is apparent that the deviation (experimental-predicted) is always negative, while at the higher pressures tested the deviations are almost always positive. This effect appears to warrant further study. With the exception of the first two results, and one 2-phase measurement at 36 bar, the deviations are less than 2%, and generally within about 1%. The estimated ac-

Table 4. Corrected Calorimeter Results

Avg. pressure bar	Outlet Temp., K	Feed composition, mole %						Fraction in vapor phase V^*	Enthalpy change cal/g-mole		
		Nitrogen	Methane	Ethane	Propane	i-Butane	n-Butane		Experimental (smoothed)	BWR prediction	% deviation
18.45	249.65	1.38	95.54	2.50	0.46	0.05	0.07	1.000	1103	1144	−3.62
18.66	238.34	1.36	95.56	2.50	0.46	0.05	0.07	1.000	1194	1227	−2.74
18.32	220.28	1.34	95.58	2.50	0.46	0.05	0.07	1.000	1394	1410	−1.13
18.25	214.53	1.49	95.16	2.76	0.51	0.03	0.05	1.000	1448	1465	−1.17
18.52	207.87	1.34	95.58	2.50	0.46	0.05	0.07	1.000	1513	1527	−0.92
18.31	201.70	1.40	95.15	2.80	0.54	0.05	0.06	1.000	1565	1573	−0.51
17.97	200.17	1.34	95.58	2.50	0.46	0.05	0.07	1.000	1609	1624	−0.94
18.87	196.69	1.34	95.58	2.50	0.46	0.05	0.07	1.000	1639	1643	−0.25
18.94	196.50	1.34	95.58	2.50	0.46	0.05	0.07	1.000	1636	1646	−0.63
18.96	196.50	1.36$^{\times}$	95.58$^{\times}$	2.58$^{\times}$	0.44$^{\times}$	0.02$^{\times}$	0.03$^{\times}$	0.988	1639	1643	−0.37
		1.15^{+}	84.11^{+}	5.01^{+}	4.46^{+}	1.69^{+}	3.58^{+}	—	—	—	—
18.40	189.55	1.44$^{\times}$	95.34$^{\times}$	2.73$^{\times}$	0.44$^{\times}$	0.02$^{\times}$	0.03$^{\times}$	0.995	1684	1703	−1.13
		0.93^{+}	68.66^{+}	10.12^{+}	11.93^{+}	3.23^{+}	5.14^{+}	—	—	—	—
18.19	188.03	1.46$^{\times}$	95.42$^{\times}$	2.69$^{\times}$	0.40$^{\times}$	0.01$^{\times}$	0.02$^{\times}$	0.996	1699	1720	−1.23
		0.08^{+}	30.32^{+}	22.87^{+}	27.93^{+}	6.75^{+}	12.05^{+}	—	—	—	—
35.96	242.80	1.37	95.54	2.51	0.46	0.05	0.07	1.000	1274	1275	−0.02
36.14	237.90	1.39	95.24	2.76	0.51	0.04	0.06	1.000	1346	1335	+0.79
35.28	220.00	1.44	95.11	2.80	0.54	0.05	0.06	1.000	1526	1511	+0.98
36.25	216.88	1.45	95.08	2.81	0.55	0.05	0.06	1.000	1566	1551	+0.96
36.11	210.21	1.44	95.17	2.76	0.51	0.05	0.07	1.000	1658	1644	+0.84
35.07	202.28	1.42	95.13	2.80	0.54	0.05	0.06	1.000	1748	1730	+1.03
36.18	188.88	1.49$^{\times}$	95.68$^{\times}$	2.46$^{\times}$	0.33$^{\times}$	0.01$^{\times}$	0.02$^{\times}$	0.974	2084	2087	−0.17
		0.56^{+}	76.68^{+}	12.41^{+}	7.39^{+}	1.13^{+}	1.83^{+}	—	—	—	—
35.75	188.48	1.36$^{\times}$	95.95$^{\times}$	2.30$^{\times}$	0.32$^{\times}$	0.03$^{\times}$	0.04$^{\times}$	0.980	2128	2080	+2.25
		0.32^{+}	70.84^{+}	14.80^{+}	9.00^{+}	1.79^{+}	3.26^{+}	—	—	—	—
35.89	173.49	2.04$^{\times}$	97.09$^{\times}$	0.80$^{\times}$	0.05$^{\times}$	0.01$^{\times}$	0.01$^{\times}$	0.361	3170	3184	−0.44
		0.87^{+}	94.90^{+}	3.41^{+}	0.64^{+}	0.08^{+}	0.10^{+}	—	—	—	—
56.17	237.78	1.39	95.17	2.80	0.53	0.05	0.06	1.000	1450	1435	+1.03
56.50	234.79	1.45	95.38	2.59	0.45	0.05	0.07	1.000	1496	1477	+1.27
56.99	225.91	1.33	95.42	2.63	0.49	0.06	0.07	1.000	1631	1609	+1.35
56.59	213.99	1.41	95.17	2.76	0.51	0.05	0.06	1.000	1841	1820	+1.14
56.57	207.28	1.37	95.38	2.67	0.48	0.05	0.08	1.000	1997	1995	+0.09
56.78	205.38	1.33	95.36	2.67	0.51	0.06	0.07	1.000	2043	2076	−1.59
56.71	199.91	1.34	95.40	2.65	0.48	0.05	0.07	1.000	2526	2489	+1.46
56.43	188.64	1.47$^{\times}$	95.76$^{\times}$	2.27$^{\times}$	0.40$^{\times}$	0.05$^{\times}$	0.05$^{\times}$	0.118	2902	2857	+1.55
		1.31^{+}	95.29^{+}	2.72^{+}	0.54^{+}	0.06^{+}	0.08^{+}	—	—	—	—

* Determined from the measured phase compositions.
× = vapor phase.
+ = liquid phase.

curacy of the measurements (±0.9%) would appear to be substantiated, while the modified BWR equation would appear satisfactory for design purposes in the range tested.

ACKNOWLEDGMENT

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NOTATION

A_0, B_0, C_0, a, b, c = constants in the BWR equation
K = equilibrium ratio
L = parameter in the mixing equations
M_{ij} = interaction parameter introduced by Orye
P = pressure (note that 1 atm = 1.013 bar)
q = constants in the correlating equation for R_{ij}
R_{ij} = repulsion factor for use in the mixing equation
T = temperature
x = mole fraction, liquid or vapor
α, γ = constants in the BWR equation

Subscripts

c = critical properties
i, j, k = for components i, j or k

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Interpretation of Overall Area Tests for Thermodynamic Consistency: The Effect of Random Error

Methods are developed and illustrated for determining the amount of nonsatisfaction of the overall area (integrated Gibbs-Duhem equation) test for vapor-liquid equilibrium data that is to be expected on the basis of random experimental uncertainties. Data which satisfy the overall test within these limits, as well as the local area test, are said to be consistent within the bounds established by their experimental uncertainties, while data which do not are said to show significant systematic error and hence are termed inconsistent.

MICHAEL R. SAMUELS

Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

DEAN L. ULRICHSON
and F. DEE STEVENSON

Department of Chemical Engineering
Iowa State University
Ames, Iowa 50010

SCOPE

Experimental vapor-liquid data are frequently checked for internal consistency by means of the Gibbs-Duhem equation (either in its differential or integral form). Unfortunately, no set of vapor-liquid data will exactly satisfy the Gibbs-Duhem equation. Such lack of agreement may arise from systematic errors due to failure of the experimental procedure or instrumentation and random experimental uncertainties because of the finite resolution of the experimental measurements. Although random measurement uncertainties may lead in many cases to the same form of incorrect results as do systematic errors, a set of data which are subject to essentially random uncertainties should not be rejected as inconsistent because they do not satisfy the Gibbs-Duhem equation. One may legitimately claim that these random uncertainties make the data of questionable value (particularly if there are insufficient data to allow the experimental uncertainties to be reduced by statistical averaging techniques). But this is a considerably different statement than saying that the data are inconsistent. The inconsistent label should be applied only to those data which exhibit systematic error. These data are of considerably lower value since no averaging techniques are capable of reducing the effects of systematic errors. A previous paper describes the propagation of experimental uncertainties in the application of the differential Gibbs-Duhem equation. In this paper a procedure is developed for determining the nonsatisfaction of the integral Gibbs-Duhem equation that is attributable solely to random experimental uncertainties. Data which show significantly more nonsatisfaction than this are termed inconsistent. The procedure is illustrated by application to ten sets of experimental vapor-liquid equilibrium data selected from the literature.