Solvent Losses in Gas Absorption. Solubility of Methanol in Compressed Natural and Synthetic Gases

Experimental results are reported for the solubility of methanol in compressed nitrogen, methane, ethane and carbon dioxide in the region −45° to +10°C and 17 to 62 bars.

New and previously published experimental data are used to obtain (or estimate second virial coefficients for all binary pairs in mixtures containing hydrogen, nitrogen, carbon monoxide, methane, ethane, propane, carbon dioxide, hydrogen sulfide and methanol. These coefficients, combined with experimental data for the vapor pressure of methanol and with Henry's constants, partial molar volumes and Margules coefficients for dissolved gases in methanol, yield a correlation for calculating solvent losses as a function of temperature, pressure and gas composition. For a large-scale natural-gas absorption process, these losses may represent a significant economic factor in plant design.

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SCOPE

In a large-scale absorption process, the solubility of the solvent in the effluent gas may be sufficiently large to represent a significant economic loss. At low pressures, this solubility is determined primarily by the solvent's vapor pressure, but at advanced pressures, gas phase nonideality also is important. In most cases, this nonideality increases solvent loss, often very much so. This work concerns the solubility of a common solvent, methanol, in gaseous mixtures typically encountered in a natural and synthetic gas sweetening process. Some new experimental solubility data are reported. New and previously published experimental results are subjected to a molecular-thermodynamic analysis. This analysis leads to a correlation which enables the design engineer to calculate methanol losses as a function of temperature, pressure and gas composition.

CONCLUSIONS AND SIGNIFICANCE

When limited but well-chosen experimental solubility data are interpreted along molecular-thermodynamic lines, it is possible to establish a theoretically based correlation useful for interpolation and extrapolation. Such a correlation is given here for calculating the solubility of methanol in gaseous mixtures in the region −90° to +40°C and pressures to (about) 80 bars. Because of this solubility, methanol losses in a large-scale absorption process may be appreciable. In a gas-sweetening process with a throughput of about 3 million m^3/day, the cost of methanol loss may be several million dollars per year.

Removal of carbon dioxide and hydrogen sulfide from sour natural or synthetic gases is commonly achieved by absorption using a selective solvent. To obtain large solubilities in the solvent, absorption is often carried out at low temperatures and advanced pressures.

Since the solvent is not totally involatile, some solvent leaves the absorber with the sweetened gas. While the concentration of vaporized solvent in the sweetened gas is usually very small, the large throughput encountered in typical industrial-scale, natural-gas plants may produce a solvent loss which is economically significant. Careful design and economic evaluation of an absorption absorption process requires reliable estimates of solvent loss.

To facilitate such estimates, this work describes, first, experimental studies to determine the solubility of methanol in compressed nitrogen, methane, ethane and carbon dioxide and, second, a thermodynamic analysis of new as well as previously reported experimental results. Finally, for absorption process design, a correlation is presented for calculating methanol losses as a function of temperature, pressure and effluent gas composition.

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EXPERIMENTAL

The experimental apparatus is similar to that used by Benson (1959), Rigby (1968) and D'Avila and Kaul (1976). Some modifications were made for operation at lower temperatures and for determination of gas phase compositions by liquid-gas chromatography.

Figure 1 shows a schematic diagram of the flow method solubility apparatus. Two cells, partially filled with methanol, are connected in series to assure saturation; each cell contains a stainless steel sparger with an average pore size of 5 μ. Gas bubbles slowly through the liquid. Saturated gas leaving the second cell is expanded and flows through a heated line to the cold trap where the condensable component is removed. This trap is cooled by a mixture of acetone and dry ice, maintained at −80°C. for experiments with methane and nitrogen and at −30°C. for experiments with ethane and carbon dioxide. The volume of gas flowing through the cold trap is measured with a calibrated wet test meter; accuracy of volume measurement is within 0.2%. Since the flow rate of the gas after expansion is here always less than 30 cm^3/min, it is unlikely that liquid in the cells is entrained with the gas. However, to eliminate possible entrainment, several layers of glass beads, supported by a perfo-

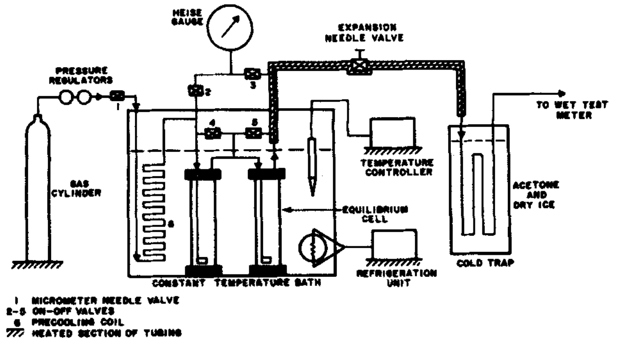

Figure 1. Schematic diagram of solubility apparatus.

TABLE 1. SOLUBILITY OF METHANOL (1) IN COMPRESSED GASES (2)

Component 2	Temperature, °C	Total Pressure, bars	Vapor phase mole fraction $y_1 \times 10^5$
Nitrogen	10	38.40	274.2
	10	59.38	208.0
	−22.5	38.60	36.78
	−22.5	59.48	32.00
	−45.6	38.60	6.11
	−45.6	59.38	5.95
	−45.6	61.20	5.60
Ethane	5	22.04	345.1
	5	22.04	350.8
	−6	19.11	203.4
	−6	19.45	202.2
Methane	0	46.06	166.9
	0	46.40	164.6
	22.5	57.12	54.13
	−45.6	41.40	12.03
	−45.6	41.54	11.94
	−45.6	56.81	15.04
Carbon dioxide	0	17.56	336.6
	0	17.83	332.9
	−10	17.23	203.3
	−10	17.52	192.6

rated stainless steel disk, were placed just before the outlet of each cell. The solubility data reported here are independent of flow rate, provided that rate is less than 30 cm^3/min.

The equilibrium cells are placed in an agitated, constant temperature bath controlled by a Hallikainen thermotrol. Temperatures were measured by thermometers calibrated with National Bureau of Standards thermometers; the estimated accuracy is within ±0.2°C. Ethanol is the bath fluid for all measurements.

The pressure is measured with a Bourdon type Heise gauge calibrated with an Aminco dead weight gauge. The uncertainty in pressure is ±0.14 bar. The influence of these and other experimental uncertainties is discussed later.

Materials

Methane, ethane and carbon dioxide have a reported minimum purity of 99.97, 99 and 99.8%, respectively, while nitrogen has a reported minimum purity of 99.996% by volume. Methanol has a reported purity of 99.9%.

Gas Analysis

In previous studies reported from this laboratory (Benson, 1959; Rigby, 1968; D'Avila and Kaul, 1976), the amount of condensate collected was determined gravimetrically. However, for methanol at the low temperatures used in the present study, the vapor pressures are so small that no accurately weighed amount of condensate can be collected in a reasonable time. Therefore, a Beckman gas chromatograph (Model GC-2A, with thermal conductivity detector) and a Wheelco 1 m.v. span recorder connected to a digital integrator (Minigrator, Spectra-Physics Inc.) were used to detect and record the concentration of solute in samples taken from the cold trap.

Calibrations were made in the concentration range 10 to 500 μmole methanol/cm^3 of solution, using n-propanol as internal standard at a constant concentration of 50 μmole/cm^3 of solution. The column packing was Porapak Q. The length of the column was 183 cm, and its temperature was 190°C for all measurements. Helium was the carrier gas, and the filament current was 200 mA. The flow rate of the carrier gas was 50 cm^3/min, and the sample size was 5 μl, except at the lowest temperature, when the sample size was 10 μl. The digital integrator, used to measure peak area ratios, gave excellent reproducibility.

For replication, three samples were injected into the gas chromatograph; peak area ratios were measured for each sample. Reproducibility was always within ±1.5%. No change in peak area ratio was observed by using smaller sample sizes. Sample injections for calibrations and for condensates were made at the same operating conditions.

The equilibrium mole fraction of methanol in the vapor phase was determined from the gas flow rate, the amount of methanol collected in the cold trap and the time required to collect that amount.

Results

Solubility data were obtained for methanol in compressed methane, ethane, carbon dioxide and nitrogen in the temperature range −45.6° to ±10°C. and for the pressure range 17 to 62 bars. Detailed results are given in Table 1.

THERMODYNAMIC ANALYSIS

The essence of this analysis is to relate the experimentally measured solubility of methanol to its fugacity coefficient in the gas mixture and to relate that to the second virial coefficient B_{12}. At temperature T and total pressure P, the equilibrium relation for methanol (1) is

$$f_1^V = f_1^L \tag{1}$$

The fugacity of the vapor phase is related to vapor phase mole fraction y_1 by

$$f_1^V = y_1 \phi_1 P \tag{2}$$

The fugacity of methanol in the liquid phase is related to the liquid phase mole fraction x by

$$f_1^L = \gamma_1 \phi_1^s x_1 P_1^s \exp\left\{\frac{v_1^L(P - P_1^s)}{RT}\right\} \tag{3}$$

Equation (3) assumes that v_1^L depends only on temperature, not on pressure.

If we substitute Equations (2) and (3) into Equation (1) and note that $x_1 = 1 - x_2$, fugacity coefficient ϕ_1 is related to mole fractions y and x by

$$\phi_1 = \frac{\gamma_1(1 - x_2)P_1^s\phi_1^s \exp\left\{\dfrac{v_1^L(P - P_1^s)}{RT}\right\}}{y_1 P} \tag{4}$$

where 2 refers to the light component. Activity coefficient γ_1 is given by the two-suffix Margules equation

$$\ln \gamma_1 = \frac{A}{RT} x_2^2 \tag{5}$$

Since x_2 is small, γ_1 is near unity. Evaluation of fugacity coefficient ϕ_1, therefore, is insensitive to the value of Margules constant A.

Solubility x_2 was calculated using the Kritchevsky-Iliinskaya equation (Prausnitz, 1969):

TABLE 2. EXPERIMENTAL SECOND VIRIAL CROSS COEFFICIENTS B_{12} FOR BINARY MIXTURES OF METHANOL (1) WITH NITROGEN, METHANE, ETHANE AND CARBON DIOXIDE

Component (2)	Temperature, °K	B_{12}, cm^3/g mole
Nitrogen	283.2	−91 ± 9
	250.7	−136 ± 8
	227.6	−175 ± 11
Ethane	278.2	−331 ± 17
	267.2	−376 ± 8
Methane	273.2	−171 ± 10
	250.7	−264 ± 6
	227.6	−373 ± 9
Carbon dioxide	273.2	−465 ± 16
	263.2	−584 ± 31

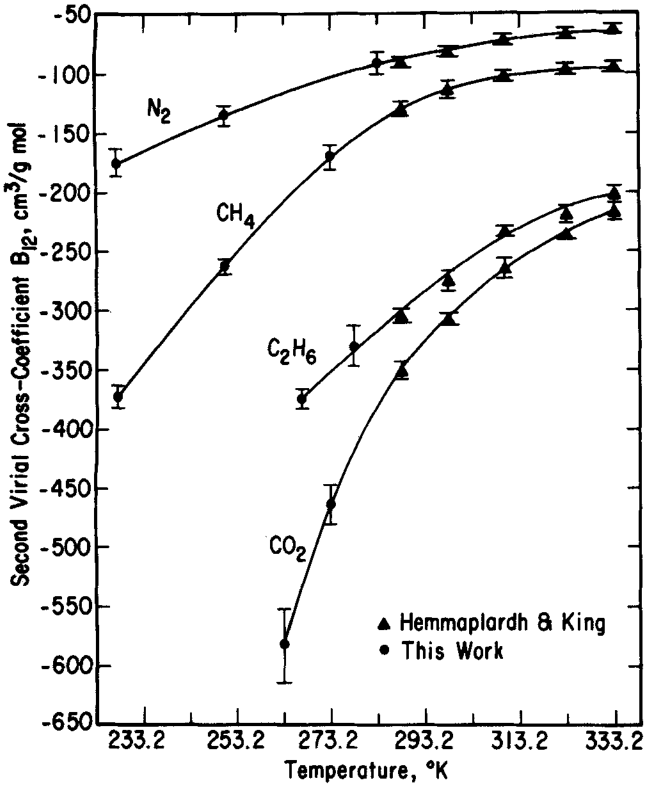

Figure 2. Second virial cross-coefficients for binary mixtures of methanol with nitrogen, methane, ethane and carbon dioxide.

$$\ln \frac{f_2}{x_2} = \ln H_{2,1}^{(P_1^s)} + \frac{A}{RT}(x_1^2 - 1) + \frac{v_2^{-\infty}(P - P_1^s)}{RT} \qquad (6)$$

where $H^{(P_1^s)}$ is Henry's constant at saturation pressure P_1^s, and $v_2^{-\infty}$ is the liquid phase partial molar volume at infinite dilution. Henry's constants, Margules coefficients and partial molar volumes were taken (or estimated) from the literature (Shenderei, Zel'venskii and Ivanovskii, 1961; Weber and Knapp, 1978; Landolt-Börnstein, 1976; Kritchevsky and Iliinskaya, 1945; Lyckman, Eckert and Prausnitz, 1965; Brelvi and O'Connell, 1972).

For the temperatures of interest here, the vapor pressure of methanol is very small; therefore, the fugacity coefficient ϕ_1^s is essentially unity. Vapor pressures and molar volumes for methanol were taken from the literature (Wilhoit and Zwolinski, 1973; Timmermans, 1950, 1965).

At moderate vapor phase densities such as those encountered here, the fugacity coefficient in the vapor phase is given by the virial equation

$$\ln \phi_1 = \{2(y_1B_{11} + y_2B_{12}) - B_M\}P/RT \qquad (7)$$

where B_M, the second virial coefficient of the gas mixture, is related to the gas composition by

$$B_M = y_1^2B_{11} + 2y_1y_2B_{12} + y_2^2B_{22} \qquad (8)$$

where B_{11} is the second virial coefficient of pure component 1, and B_{22} is that for pure component 2. Since $y_1 << 1$, the terms y_1B_{11} and $y_1^2B_{11}$ are negligible. Since $y_1 << y_2$, Equation (7) shows that the fugacity coefficient is very sensitive to B_{12}. Reliable measurements of y_1, therefore, are necessary to obtain accurate values for B_{12}. By using experimental values of y_1, coefficient B_{12} is readily found.

Table 2 and Figure 2 present second virial cross coefficients B_{12} for binary mixtures of methanol with nitrogen, methane, ethane and carbon dioxide. When plotted against temperature,. the low temperature data obtained here form continuous curves with results at higher temperatures reported by Hemmaplardh and King (1972).

ERROR ANALYSIS

Possible sources of significant experimental error are random errors, errors in measurement of temperature, pressure and mole fraction. Random errors were estimated from observed scatter in the data. The uncertainty in temperature arises from temperature gradients in the bath and from temperature measurements. Under worst conditions, the maximum uncertainty is ±0.2°C which produces less than 1.2% error in the vapor pressure and, from Equations (4) and (7), introduces less than 1.4% error in B_{12}.

Uncertainty in pressure measurement is less than 0.14 bar, giving an error in B_{12} of less than 0.5% at a total pressure of 17.3 bars. At higher pressures, the uncertainty in pressure measurement becomes insignificant.

Uncertainties in vapor phase mole fraction arise from wet test meter and from gas chromatographic measurements. Errors from wet test meter measurements, peak area measurements, etc., produce uncertainties of 1.5% in y_1. In most cases, this introduces an error less than 1% in B_{12}.

The second virial coefficient of pure methanol B_{11} has only a slight influence on ϕ_1 in Equation (7). An error as large as 10 000 cm^3/g mole introduces an uncertainty of less than 0.4% in B_{12} for the binary mixture nitrogen-methanol at 227.6°K and 60 bars.

CORRELATION FOR PURE COMPONENT SECOND VIRIAL COEFFICIENTS

The virial equation of state truncated after the second term is

$$z = \frac{Pv}{RT} = 1 + \frac{BP}{RT} \qquad (9)$$

where the second virial coefficient B provides a convenient source of information on the intermolecular potential function. It is possible to determine the parameters of an assumed potential model from limited second virial coefficient data; the potential may then be used for interpolation and extrapolation with respect to temperature and for guidance in the prediction of volumetric properties of similar systems. When the square-well potential is used, the second virial coefficient is

$$B = 2/3\pi N_A\sigma^3[1 - (\underline{R}^3 - 1)\{\exp(\epsilon/kT) - 1\}] \qquad (10)$$

The square-well potential is illustrated in Figure 3. Potential parameters are determined by fitting experimental to calculated second virial coefficients.

Table 3 gives potential parameters for eight pure fluids using the best compromise for a common $\underline{R}$ = 1.55. All second virial coefficient data were taken from Dymond and Smith (1969). Data which differ from the calculated curve by more than five times the $<\Delta B>$ deviation were rejected and the remaining data refitted. The maximum deviation ΔB was always less than 25 cm^3/g mole.

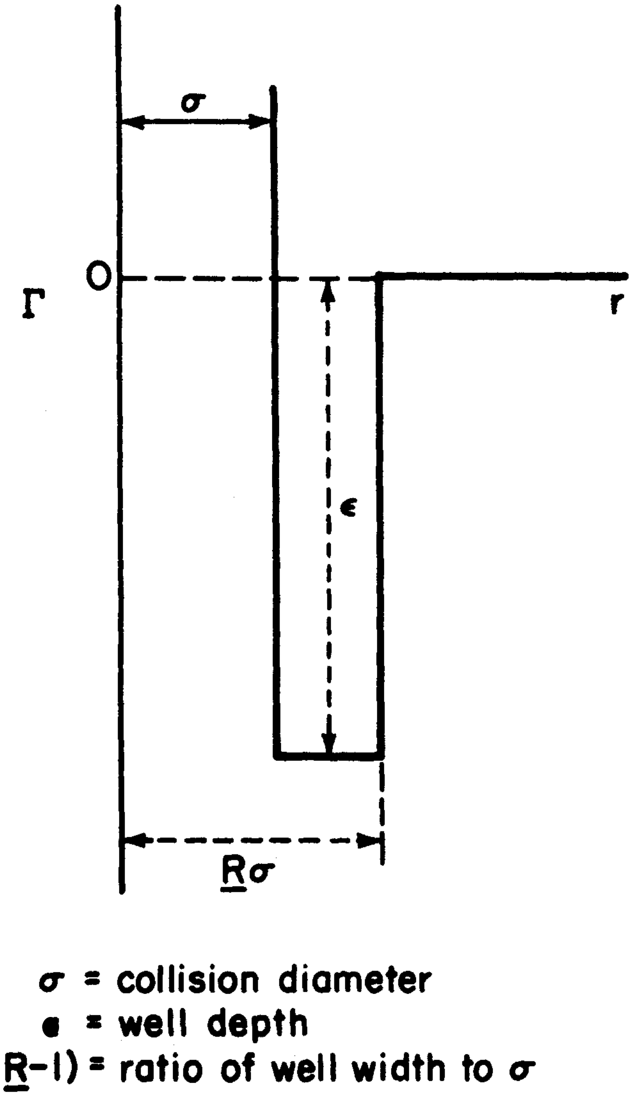

Figure 3. Square-well potential Γ.

It was not possible to fit the limited data for methanol using $\underline{R} = 1.55$ or any other realistic set of parameters for the square-well potential. To predict the best second virial coefficient at low temperatures, the correlation of Tsonopoulos (1974) was selected from among several correlations (Hayden and O'Connell, 1975; Zubarev et al., 1973; Weltner and Pitzer, 1951). At low temperatures (for example, −80°C), the predicted second virial coefficients differ markedly, depending on the correlation used. Fortunately, for methanol only a rough estimate of B is needed, since the lower the temperature, the lower the mole fraction of methanol in the vapor phase.

TABLE 3. SQUARE-WELL POTENTIAL PARAMETERS

Compound	σ, nm × 100	ε/k, °K	ΔB max cm³/g mole	<ΔB> cm³/g mole	Temperature range, °K
Hydrogen	25.77	34.3	0.6	0.2	98-423
Nitrogen	32.72	110.0	14.0	12.0	148-400
Methane	33.11	160.5	2.2	0.6	150-400
Carbon monoxide	33.36	107.1	2.7	0.8	173-423
Ethane	37.35	245.0	21.0	15.0	220-450
Carbon dioxide	38.42	207.9	6.0	1.0	223-477
Propane	39.15	347.0	23.0	5.8	260-470
Hydrogen sulfide	39.84	245.8	0.7	0.3	277-444

$<\Delta B> = \frac{1}{N}\sum^{N} |B_{\exp} - B_{\text{calc}}|$ where N is the number of experimental points

$\Delta B = |B_{\exp} - B_{\text{calc}}|$

Table 4 and Figures 4, 5 and 6 show calculated second virial coefficients for hydrogen, nitrogen, carbon monoxide, methane, ethane, propane, carbon dioxide, hydrogen sulfide and methanol.

SECOND VIRIAL CROSS COEFFICIENTS

For methanol free mixtures, second virial cross coefficients are satisfactorily predicted using the square-well potential with conventional mixing rules. For B_{ij}, Equation (10) is used with

$$\underline{R}_{ij} = 1.55 \tag{11}$$

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{12}$$

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{\frac{1}{2}} \tag{13}$$

Calculated results are in good agreement with limited experimental data (Hayden and O'Connell, 1975; Brewer, 1967).

Second virial cross coefficients for binaries containing methanol could be fitted only by using $\underline{R} = 1.2$ and a temperature dependent characteristic energy ϵ_{ij}. The smaller $\underline{R}$ is probably a direct consequence of the short-range interaction between the nonpolar (or slightly polar) component and the OH group in methanol. The need for a temperature dependent ϵ_{ij} is probably due to orientational effects; at high temperatures, orientation between the dissimilar molecules is not important (all orientations are equally probable), but at low temperatures the energetically stronger interaction (molecule ↔ OH CH_3) is favored; ϵ_{ij} rises as the temperature falls.

TABLE 4. SECOND VIRIAL COEFFICIENTS FOR PURE FLUIDS, CM³/G MOLE

Temperature, °C	H_2	N_2	CO	CH_4	C_2H_6	C_3H_8	CO_2	H_2S	CH_3OH
60	15.2	−2.9	−1.5	−31.4	−129	−302	−97	−157	−1 020
50	15.0	−4.6	−3.3	−34.4	−137	−322	−104	−168	−1 234
40	14.8	−6.5	−5.2	−37.7	−147	−343	−112	−179	−1 515
30	14.5	−8.5	−7.2	−41.3	−156	−366	−120	−192	−1 891
20	14.3	−10.6	−9.4	−45.1	−168	−392	−130	−205	−2 400
10	14.0	−13.0	−11.6	−49.3	−181	−420	−140	−221	−3 098
0	13.7	−15.5	−14.4	−53.9	−194	−453	−151	−237	−4 068
−10	13.4	−18.3	−17.2	−59.0	−209	−489	−163	−256	−5 432
−20	13.1	−21.3	−20.3	−64.6	−226	−530	−177	−277	−7 379
−30	12.7	−24.7	−23.8	−70.8	−246	−577	−192	−300	−10 198
−40	12.3	−28.4	−27.5	−77.8	−267	−631	−209	−327	−14 344
−50	11.8	−32.5	−31.7	−85.5	−292	−694	−228	−357	−20 540
−60	11.3	−37.1	−36.4	−94.3	−320	−768	−250	−391	−29 963
−70	10.8	−42.3	−41.7	−104.3	−353	−856	−276	−432	−44 572
−90	9.5	−54.9	−54.5	−129.1	−437	−1 089	−340	−534	−105 122

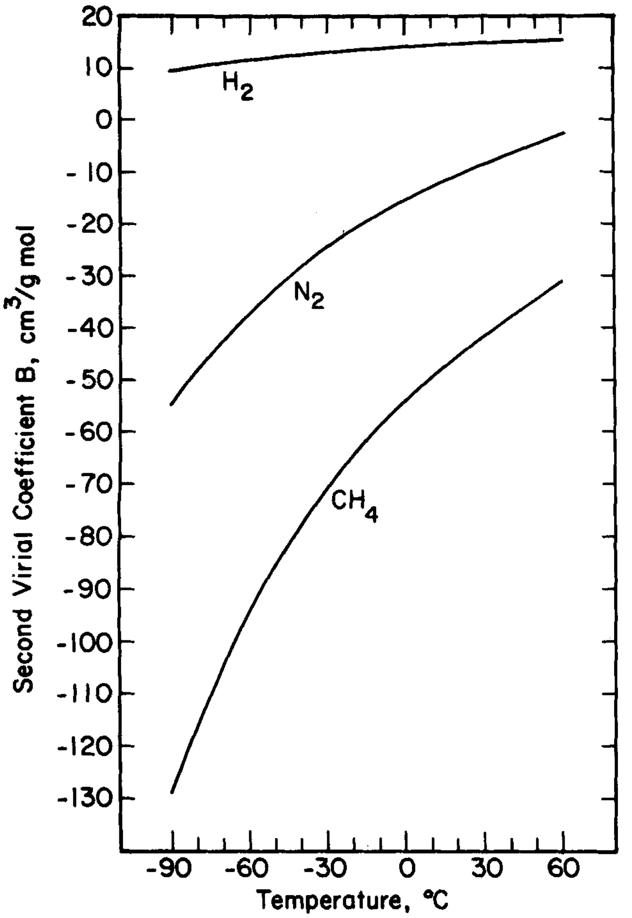

Figure 4. Second virial coefficients calculated with the square-well potential. Pure fluids.

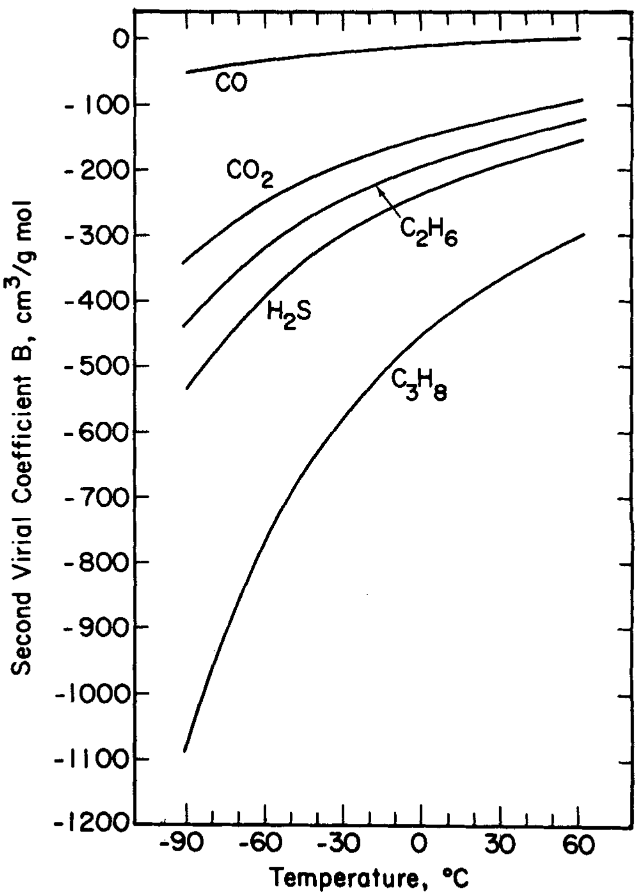

Figure 5. Second virial coefficients calculated with the square-well potential. Pure fluids.

Equation (10) is again used, but Equation (13) is modified to

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{\frac{1}{2}}\left(1 + \frac{c}{T}\right) \tag{14}$$

Analyzing together all B_{ij} data for methanol binaries, $c = 125$ for mixtures with nonpolar nitrogen, ethane and methane, and $c = 185$ for mixtures with quadrupolar carbon dioxide. For mixtures with nonpolar hydrogen and carbon monoxide, we also set $c =$

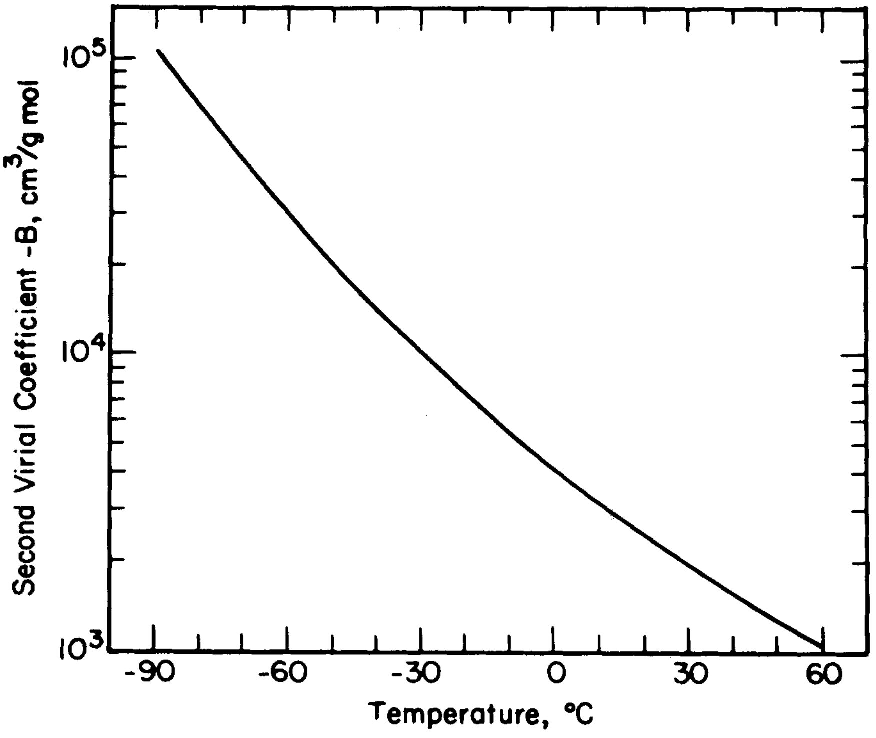

Figure 6. Second virial coefficients for methanol calculated with Tsonopoulos' correlation.

Table 5. Parameter c and Deviations from Experimental for Calculated Second Virial Cross Coefficients, Four Binary Mixtures Containing Methanol

Second component	c, °K	$\lvert\Delta B\rvert$ max*, cm³/g mole	$<\Delta B>$*, cm³/g mole	Temperature range, °K
Nitrogen	125	23.5	10.6	228-333
Ethane	125	23.8	10.1	268-333
Methane	125	25.0	12.4	228-333
Carbon dioxide	185	21.0	10.3	266-333

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* See Table 3.

125. For mixtures with slightly polar hydrogen sulfide, we set c = 185.

As shown in Table 5, a good fit is obtained when we use for methanol the reasonable values $\epsilon/k = 810°K$ and $\sigma = 0.355$ nm.

Table 6 and Figures 7 and 8 show calculated second virial cross coefficients for eight binary mixtures containing methanol.

CALCULATION OF SOLVENT LOSSES IN ABSORPTION

The correlation described above provides a basis to calculate methanol losses in a multicomponent mixture of gases as a function of temperature, pressure and gas composition.

Table 6. Second Virial Cross Coefficients for Binary Methanol-Gas Systems, cm³/g mole

Temperature, °C	H_2	CO	N_2	CH_4	C_2H_6	C_3H_8	CO_2	H_2S
60	10	−38	−38	−76	−174	−313	−205	−278
50	9	−44	−45	−86	−195	−351	−231	−314
40	7	−51	−52	−98	−219	−397	−263	−357
30	5	−59	−60	−111	−248	−452	−300	−409
20	3	−68	−69	−126	−282	−517	−345	−471
10	1	−79	−80	−144	−323	−596	−399	−548
0	−2	−92	−93	−166	−373	−695	−466	−644
−10	−5	−106	−108	−192	−434	−819	−550	−765
−20	−8	−124	−126	−223	−510	−977	−657	−921
−30	−12	−146	−147	−262	−606	−1 183	−795	−1 126
−40	−17	−172	−174	−311	−730	−1 457	−979	−1 403
−50	−22	−205	−207	−373	−894	−1 831	−1 230	−1 786
−60	−29	−247	−250	−455	−1 117	−2 357	−1 581	−2 334
−70	−37	−301	−305	−564	−1 428	−3 121	−2 090	−3 146
−80	−47	−373	−378	−715	−1 877	−4 277	−2 859	−4 404
−90	−59	−472	−479	−930	−2 552	−6 112	−4 080	−6 453

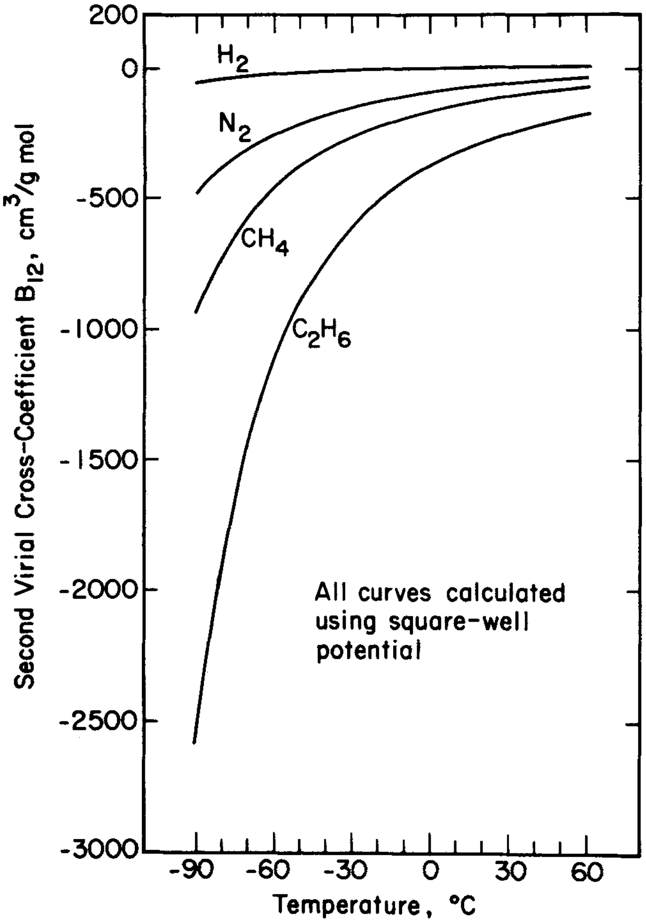

Figure 7. Second virial cross-coefficients for binary methanol (1)—gas (2) systems.

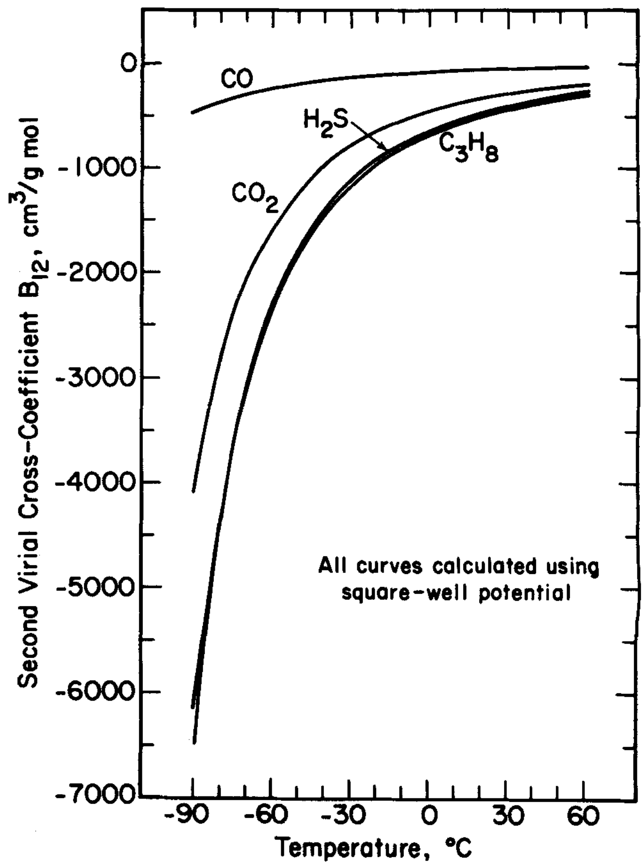

Figure 8. Second virial cross-coefficients for binary methanol (1)—gas (2) systems.

TABLE 7. HENRY'S CONSTANTS, MARGULES CONSTANTS AND PARTIAL MOLAR VOLUMES FOR SOLUTES IN METHANOL

	$a^{(0)}$	$a^{(1)}$	$a^{(2)} \times 10^{-5}$	Temperature range, °C	% error in Henry's constant	Margules constant A, cm³-bar/g mole*	$\bar{v}^{\infty}$, cm³/g mole*
H_2	7.4133	399.818	0	−60/40	1	33 400	35
N_2	6.7094	801.358	−1.0454	−60/25	2	28 400	47
CH_4	8.7260	−494.180	0	−60/50	4	23 300	47
C_2H_6	11.3411	−1665.374	0	−80/25	4	19 300	56
C_3H_8	4.6759	1513.570	−4.6805	−45/40	5	13 200	76
CO	8.6861	−238.794	0	−80/40	4	28 400	47
CO_2	7.9908	−213.290	−2.1070	−75/25	4	12 200	40
H_2S	11.3789	−2285.560	0	−80/30	4	8 100	39

* Evaluated (estimated) at 0°C.

Assuming that equilibrium prevails at the top of the absorption column, the vapor phase fugacity is related to the vapor phase mole fraction by

$$f_i^V = \phi_i y_i P \tag{15}$$

where the fugacity coefficient ϕ_i is given by

$$\ln \phi_i = \Big(2\sum_j y_j B_{ij} - B_M\Big) P/RT \tag{16}$$

where

$$B_M = \sum_i \sum_j y_i y_j B_{ij} \tag{17}$$

For methanol (designated by subscript 1), the liquid phase fugacity is given by Equation (3). For all other components, the liquid phase fugacity is given by

$$f_i^L = \gamma_i^* \; x_i H_{i,1}^{(P_1^s)} \exp\left\{\frac{\bar{v}_i(P - P_1^s)}{RT}\right\} \tag{18}$$

The activity coefficient γ_i^* is normalized such that $\gamma_i^* \rightarrow 1$ as $x_i \rightarrow 0$ and $x_1 \rightarrow 1$.

Since x_i is small ($i \neq 1$), we use the approximation $\bar{v}_i(T, x) = \bar{v}_i(T, x_i = 0) = \bar{v}_i^{\infty}$. Equation (18) assumes also that $\bar{v}_i$ is not pressure dependent.

We now consider a mixture containing methanol and m-1 gaseous components. There are m equations of equilibrium: Equations (2) and (3) for methanol and m-1 equations of the form

$$(i = 2, 3, 4. \ldots) \qquad \phi_i y_i P = \gamma_i^* x_i H_{i,1}^{(P_1^s)} \exp\left\{\frac{\bar{v}_i^{\infty}(P - P_1^s)}{RT}\right\} \tag{19}$$

The m equations of equilibrium contain $2m$ unknowns: m values of x and m values of y. In addition, however, we have two conservation equations ($\Sigma x = 1$ and $\Sigma y = 1$) and m-2 equations of the form y_i/y_j = constant, where neither i nor j = 1. The number of unknowns therefore is equal to the number of independent equations.

For a multicomponent liquid mixture containing one solvent in excess (methanol) and m-1 solutes, we assume that the molar excess Gibbs energy (unsymmetric convention) is given by the two-suffix Margules equation

$$g^{E*} = -\sum_{i=2}^{m} \sum_{j=2}^{m} A_{ij} x_i x_j \tag{20}$$

The activity coefficient (γ_1 or γ_i^*) is found from

$$\ln \gamma_i = \left[\frac{\partial n_T g^{E*}}{\partial n_i}\right]_{T,P,n_j} \tag{21}$$

where $n_T = \sum_i^m n_i$. For methanol, we find that

$$RT \ln \gamma_1 = -g^{E*} \tag{22}$$

and for any solute i

$$RT \ln \underset{i\neq 1}{\gamma_i^*} = -\sum_{j=2}^{m} \Big[(A_{ij}x_i + 2A_{ij}\,x_1)x_j + \sum_{\substack{ii=2 \\ ii\neq i}}^{m} (2A_{ij} - A_{ii,j})x_{ii}x_j\Big] \tag{23}$$

TABLE 8. VAPOR PRESSURE OF METHANOL

	Low temperature	High temperature
C_1	−56.137716	−56.137716
C_2	−781.158800	−7 053.270000
C_3	−93.392040	141.602400
C_4	4.249923 × 10^{-3}	4.249923 × 10^{-3}
C_5	−1.490418 × 10^{-6}	−5.202764 × 10^{-5}
C_6	10.009790	12.942710
Temperature range, °C	−97.6/−33.75	−33.75/70
Max. ΔP, bar*	1.4 × 10^{-7}	3.5 × 10^{-4}

*ΔP = Pexp − Pcalc|.

Using literature data (Shenderei and Zel'venskii, 1961; Landolt-Börnstein, 1976), we have estimated approximate Margules constants for eight solutes in methanol. For a pair of solutes in methanol, we use the rough rule

$$A_{ij} = \frac{A_{ii} + A_{jj}}{2} \; (i, j \neq 1) \tag{24}$$

Table 7 gives estimates of Margules constants. Fortunately, since methanol is present in excess, calculated results for solvent loss are insensitive to values of Margules constants. The important quantities are the vapor pressure of methanol and the values of second virial cross coefficients for binaries containing methanol.

EFFLUENT GAS COMPOSITION

At the top of the absorber, the effluent methanol free gas composition is known for every component. This methanol free composition can be related to the equilibrium gas-phase mole fraction through

$$y_i = (1 - y_1)y_i' \; i = 2, 3, \ldots\ldots m \tag{25}$$

HENRY'S CONSTANT AND PARTIAL MOLAR VOLUMES

Henry's constants were taken directly from the literature or were obtained from binary data reduction. Henry's constants are represented by the empirical equation

TABLE 9. SOLUBILITY OF METHANOL IN COMPRESSED GASES

	Temperature, °C	Pressure, bars	Mole fraction methanol y_1 Ideal	Mole fraction methanol y_1 This work	$K_1 = \frac{y_1}{x_1}$
	−90	30	2.14×10^{-7}	3.56×10^{-6}	3.7×10^{-6}
		80	8.01×10^{-8}	1.85×10^{-4}	2.0×10^{-4}
Case I	−60	30	9.63×10^{-6}	3.13×10^{-5}	3.2×10^{-5}
		80	3.61×10^{-6}	8.70×10^{-5}	9.3×10^{-5}
	−30	30	1.49×10^{-4}	2.73×10^{-4}	2.8×10^{-4}
		80	5.59×10^{-5}	2.84×10^{-4}	3.0×10^{-4}
	−30	30	1.49×10^{-4}	3.39×10^{-4}	4.0×10^{-4}
		80	5.59×10^{-5}	6.03×10^{-4}	7.3×10^{-4}
Case II	0	30	1.29×10^{-3}	2.07×10^{-3}	2.2×10^{-3}
		80	4.82×10^{-4}	1.81×10^{-3}	2.1×10^{-3}

$$\ln H = a^{(0)} + \frac{a^{(1)}}{T} + \frac{a^{(2)}}{T^2} \tag{26}$$

here T is in degrees Kelvin, and H is in bars. Table 7 gives parameters $a^{(0)}$, $a^{(1)}$ and $a^{(2)}$.

Partial molar volumes were taken from the literature or estimated from the correlation of Lyckman, Eckert and Prausnitz (1965). The density of liquid methanol is given by Wilhoit and Zwolinski (1973).

VAPOR PRESSURE OF METHANOL

Vapor pressure data for methanol are most conveniently related to temperature by an empirical equation of the form:

$$\ln P_1^s = C_1 + \frac{C_2}{C_3 + T} + C_4T + C_5T^2 + C_6 \ln T \tag{27}$$

where T is in degrees Kelvin, and C_1, C_2, C_3, C_4, C_5 and C_6 are empirical constants. Here P_1^s has units of bars. Two sets of empirical constants were necessary to fit the experimental data in the range −97.6° to 70°C. The two sets of parameters give almost the same vapor pressure between −35° to −25°C. The point of intersection of the curves produced by each set of parameters is −33.75°C, and at this point the slopes of both curves are essentially the same. Table 8 gives the two sets of parameters.

CALCULATED SOLVENT LOSSES

Having determined all the interaction parameters, we may calculate vapor-liquid equilibria for a multicomponent methanol-solute system. For m components, there are m nonlinear equations that must be solved simultaneously using an iterative Newton-Raphson technique. Calculations were performed utilizing a computer program METSOL as described elsewhere (Lazalde-Crabtree, 1979).

To illustrate how the solubility of methanol changes as a function of temperature, pressure and effluent gas composition, Figures 9 and 10 show the mole fraction of methanol for −90° to + 40°C and for pressures from 1 to 80 bars. Figure 9 shows the solubility of methanol in a mixture of light gases. Figure 10 shows the solubility of methanol in a mixture of gases containing methane, ethane and small amounts of propane, carbon dioxide and hydrogen sulfide.

The solubility of methanol is larger for the second gas mixture because some of the B_{1i} coefficients are (numerically) larger than those for the first mixture.

Table 9 gives representative values of the solubility of methanol calculated using the methods described here and also the idealized equation based on Raoult's law:

$$y_1 = \frac{x_1 P_1^s}{P} \tag{28}$$

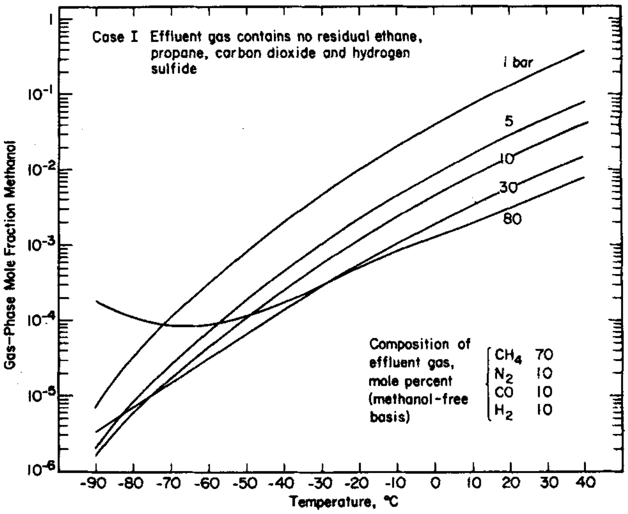

Figure 9. Solvent loss in absorption. Mole fraction methanol in effluent gas as a function of temperature and pressure.

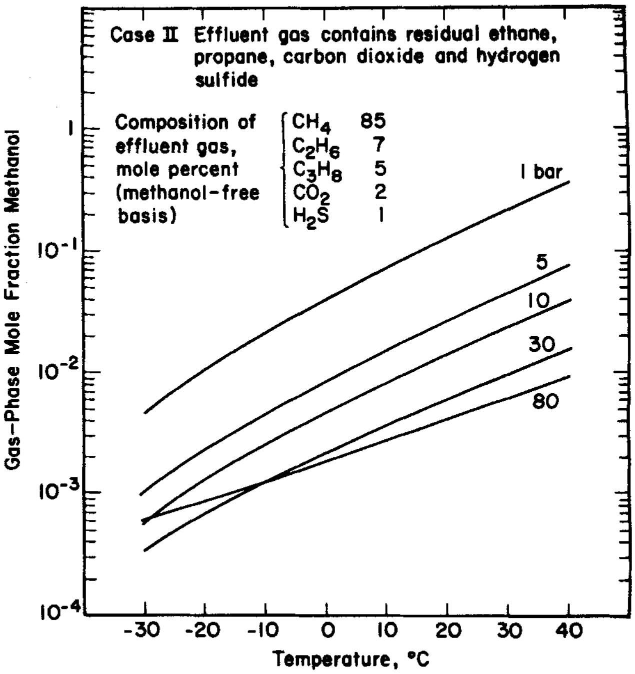

Figure 10. Solvent loss in absorption. Mole fraction methanol in effluent gas as a function of temperature and pressure.

TABLE 10. COST OF METHANOL LOSS IN THOUSANDS OF DOLLARS PER YEAR ǂ

Temperature, °C	Pressure, bars	Price of methanol, ¢/gal 45	65	85
10	5	3 346	4 833	6 320
	30	825	1 192	1 558
	80	624	901	1 178
0	10	1 013	1 463	1 913
	30	462	667	873
	80	404	584	763
−10	10	558	806	1 054
	30	272	393	514
	80	272	393	514
−30	10	132	191	250
	30	76	110	144
	80	134	194	254

ǂ Based on a gas flow rate of 10^8 (STP) ft^3 [2.83×10^6 m^3]/day.

At high pressures and low temperatures, there is a large difference showing the importance of gas phase nonideality corrections. Liquid phase corrections for nonideality are smaller, usually less than 20%.

Table 10 indicates the economic consequences of solvent loss. The results shown are for the effluent gas indicated as case II in Figure 10; the calculations are based on a flow rate of 10^8 ft^3 (STP) [2.83 × 10^6 m^3]/day.

CONCLUSION

This work presents a molecular-thermodynamic framework for the estimation of solvent losses in the effluent gas at the top of an absorber. The framework is illustrated for sweetening of sour natural gases using methanol as the absorbing liquid. Required parameters may be obtained either from binary data reduction or else from empirical correlations. No multisolute data are necessary. The calculation technique developed here is therefore readily applicable to chemical process design. Computer programs for that purpose are available.

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NOTATION

a = empirical constant in Equation (26)
A = Margules coefficient in Equation (5), cm^3 bar gmole^{-1}
B = second virial coefficient, cm^3 gmole^{-1}
c = empirical constant in Equation (14), °K
C = empirical constant in Equation (27)
f = fugacity, bar
g = Gibbs energy, cm^3 bar gmole^{-1}
H = Henry's constant, bar
$H_{i,1}^{(P_1^s)}$ = Henry's constant for component i in methanol
k = Boltzmann's constant, J °K^{-1}
K = equilibrium ratio
m = number of components
n = number of moles
N = number of experimental points
N_A = Avogadro's number, number of molecules gmole^{-1}
P = total pressure, bar
R = gas constant, cm^3 bar gmole^{-1} °K^{-1}
$\underline{R}$ = reduced well width. See Figure 3
T = absolute temperature, °K
v = molar volume, cm^3 gmole^{-1}
$\bar{v}$ = partial molar volume, cm^3 gmole^{-1}
$\bar{v}_i$ = partial molar volume of component i in methanol
x = liquid-phase mole fraction
y = vapor-phase mole fraction
y' = methanol-free vapor-phase mole fraction
z = compressibility factor

Greek Letters

Γ = potential function, J
γ = activity coefficient
r_i^* = activity coefficient of component i (unsymmetric convention)
ϵ = parameter in square-well potential, J
ϕ = fugacity coefficient
σ = parameter in square-well potential, *nm*
Δ = difference
Σ = summation

Subscripts

$i, j, 1, z, \ldots\ldots$ = components
M = mixture
T = total

Superscripts

E = excess
L = liquid phase
s = saturation
V = vapor phase
$(0), (1), (2), \ldots.$ = empirical constants
$*$ = unsymmetric convention
∞ = infinite dilution

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