# Thermodynamic Behavior of Hydrogen-Hydrocarbon Mixtures

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**By use of the Benedict-Webb-Rubin (BWR) equation of state an attempt has been made to correlate experimental vapor-liquid equilibrium data on hydrogen-methane-propane mixtures in the temperature range from 0° to —250°F. and pressure range from 500 to 1,500 lb./sq. in. abs. Considerable improvement in hydrogen *K* values has been obtained by adjusting the coefficient $\gamma$ in the BWR equation for hydrogen. In the final adjustment it was necessary to specify a new value of $\gamma$ for hydrogen at each temperature. The root-mean-square deviation of calculated from observed *K* values for hydrogen is 6.6%**

**As a further check the recommended BWR coefficients for hydrogen have been used to calculate the low-temperature hydrogen *K* values in mixtures with ethane and ethylene with good results.**

**The predicted *K* values for propane at temperatures below —150°F. have not been altered and are still in error by as much as 2 orders of magnitude.**

The expanding use of digital computing equipment in the simulation of processes has developed a strong incentive for the compact quantitative expression of physical phenomena. In the area of hydrocarbon vapor-liquid equilibrium ratios some attempts have been made to fit the experimental relationships to a curve, but an equally promising approach, for light hydrocarbons at least, is the use of an equation of state, the Benedict-Webb-Rubin (BWR) equation (*1, 2*). This equation has been used to predict from single-phase pressure-volume-temperature (*PVT*) data of pure hydrocarbons both the singular two-phase behavior and the phase behavior in multicomponent mixtures of these hydrocarbons. While considerable success has been obtained in the use of the BWR equation for mixtures of paraffins and olefins, several deficiencies in the equation have been noted in areas of its application critical to its utility. For instance, prior to this investigation it had been established that the equation would not predict satisfactorily the subatmospheric vapor pressures of pure compounds (*2*) and would not adequately represent the phase behavior of mixtures of hydrocarbons with light gases such as hydrogen (*9*), nitrogen (*5*), and carbon dioxide (*15*).

In an effort to expand the utility of the equation Benedict (*2*) suggested first that the prediction of pure-component vapor pressures at low temperatures could be improved by adjusting $C_o$ at every temperature in such a manner as to satisfy the two criteria:

$$P(d_L) = P(d_g) = P_{\text{obs.}}$$
$$f(d_L) = f(d_g)$$

The phase behavior of mixtures is predicted from the equation-of-state coefficients for pure compounds based on combining rules inferred from statistical mechanics. In cases of poor agreement with data on the phase behavior of mixtures it has been assumed that an improvement or revision of the interaction coefficients is necessary to correct the assumed combining rule. Thus Benedict and Stotler (*5*) modified the combining rule for $A_o$ in correlating *V-L* data on the nitrogen-methane system.

The prediction of the phase behavior of hydrogen-hydrocarbon mixtures is of immediate technical interest and represents one area where the BWR equation has not been too successful (*9*). It is well known that the vapor-liquid equilibrium ratios for hydrogen do not apparently follow the conventional behavior observed for mixtures of light hydrocarbons. For all temperatures above —250°F. *K* values for hydrogen decrease with increasing temperature in contrast with normal expectations, where the *K* values should increase with increasing temperature. One might suppose that such radical behavior could not possibly lend itself to prediction by the conventional equation-of-state approach; however Katz (*14*) has pointed out that this behavior of hydrogen is really only a manifestation to a larger degree of a phenomenon observed in all hydrocarbon mixtures involving very light and very heavy components.

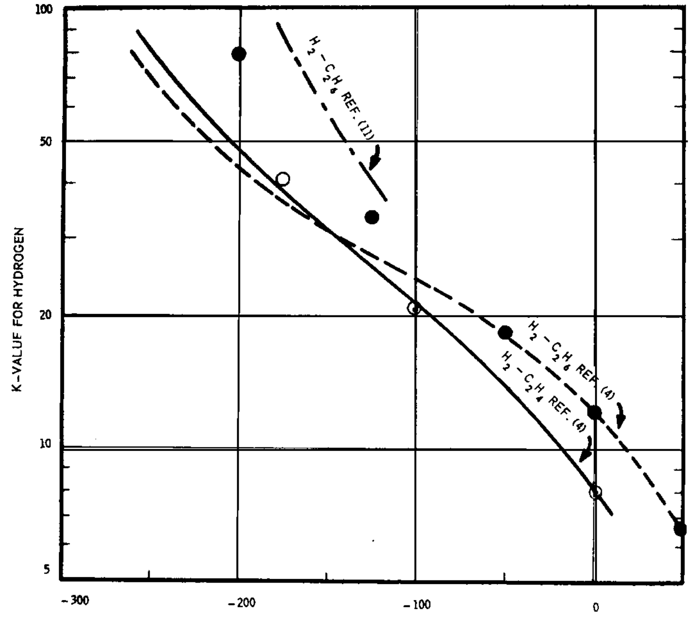

Fig. 1. Comparison of calculated *K* values with observed for hydrogen in hydrogen-ethylene and hydrogen-ethane mixtures at 1,000 lb./sq. in. abs. ● = calculated $K_{H_2}$ in hydrogen-ethane mixture, ○ = calculated $K_{H_2}$ in hydrogen-ethylene mixture.

In the light of these observations and because of the burden of calculations involved, a series of studies was undertaken with an IBM 650 to adapt the BWR equation-of-state approach to vapor-liquid equilibrium in hydrogen-hydrocarbon mixtures at low temperatures. A computer program (*20*) was available to calculate vapor-liquid equilibria from the BWR equation of state. The data employed in the study were those of Benham and Katz (*3*) for hydrogen-methane-propane mixtures. To extend the range of the hydrogen-propane binary data, two runs were selected from the Williams and Katz data (4).

Previous studies had indicated that the best available set of BWR coefficients (7) for hydrogen did not satisfactorily correlate hydrogen phase behavior. A new set of hydrogen coefficients was obtained from *PVT* data (8) over the range of interest, namely −250° to 100°F. and 0 to 2,000 lb./sq. in. abs. by means of a digital computer program (20).

To improve the prediction of pure-component vapor pressures, a general-purpose computer program for adjusting $C_o$ was developed.

The BWR equation of state approach was checked at this point in the study by evaluating the new coefficients for hydrogen and the adjusted $C_o$ values for methane and propane in the calculation of phase equilibria. Since further refinements were necessary to fit the hydrogen *K* values, the work proceeded with the objective of finding improved binary interaction coefficients from *V-L* data on binary mixtures of hydrogen methane and hydrogen propane and of using these coefficients in the calculation of the phase equilibria of ternary mixtures. It was found that improved binary interaction coefficients for hydrogen in hydrocarbon mixtures were not necessary. The behavior of hydrogen could be adequately represented by modifying $\gamma$ at each temperature.

The BWR coefficients used in the calculations for all substances other than hydrogen are those recommended by Benedict (2), with the exception that $C_o$ has been adjusted where necessary to fit the observed vapor pressure.

## RESULTS

### Fitting Hydrogen PVT

The method employed in fitting hydrogen *PVT* data is that of Brough, Schlinger, and Sage (6), where the coefficients are obtained by a least-squares fit of the *PVT* data for assumed values of $\gamma$. Several guesses are made of $\gamma$, and the value which yields the minimum standard deviation of the fit is selected as best.

A set of hydrogen coefficients had been obtained by Eubanks (7), shown in Table 1, but preliminary calculations conducted at the university laboratory indicated poor agreement between computed hydrogen *K* values with observed ones. The root-mean-square (RMS) error was 137%. Eubanks fitted hydrogen *PVT* data at temperatures below −172°F. only; therefore a new set of hydrogen coefficients was obtained with a different range of hydrogen *PVT*. The data were obtained from the same source (8) but were restricted to the range of interest, namely temperatures from 100° to −250°F. and pressures to 2,000 lb./sq. in. abs. The results of the fit of hydrogen *PVT* over the range of interest are shown in Table 1. As a by-product of the curve-fitting work, it was found that the fit of the hydrogen *PVT* over the range of interest described above was insensitive to the value of $\gamma$ over the range from 0.4 to 1.0.

One aspect of the curve-fitting results needs clarification. As was found by Eubanks, the best values of $a$ and $\alpha$ for hydrogen are negative. Such a result need not influence the ability of the BWR equation to fit the *PVT* data, but it leads to an incongruity in defining the fugacity of hydrogen in the pure state and in a mixture. Thus the coefficient for the fifth power of the density, the product $a\alpha$, is positive in the equation for the fugacity of pure hydrogen, but the corresponding term $[\alpha(a^2a_i)^{1/3} + a(\alpha^2\alpha_i)^{1/3}]$ is negative for hydrogen in a mixture. To resolve the difficulty, Eubanks suggested that the signs of $a$ and $\alpha$ be changed and that $b$ be modified to correct the third virial coefficient, $(bRT\text{-}a)$. The modified $b$ is defined by

$$b' = b + \frac{2\,|a|}{RT}$$

The results obtained in calculating *K* values with the new set of BWR coefficients for hydrogen, set 1, Table 1, were somewhat better, as indicated by a root-mean-square error of 36%.

### Adjustment of $C_o$ for Pure Substances

All calculations of *K* values described in this paper included the use of $C_o$ values which satisfactorily fit the BWR equation to the observed vapor pressures of pure substances at the temperature in question.

### Improvement in Combining Rules

The combining rules employed in deriving the BWR coefficients for a mixture are as follows:

$$\begin{aligned} B_{o_m} &= \Sigma x_i B_{o_i} \\ A_{o_m} &= [\Sigma x_i A_{o_i}{}^{1/2}]^2 \\ C_{o_m} &= [\Sigma x_i C_{o_i}{}^{1/2}]^2 \\ b_m &= [\Sigma x_i b_i{}^{1/3}]^3 \\ a_m &= [\Sigma x_i a_i{}^{1/3}]^3 \\ c_m &= [\Sigma x_i c_i{}^{1/3}]^3 \\ \alpha_m &= [\Sigma x_i \alpha_i{}^{1/3}]^3 \\ \gamma_m &= [\Sigma x_i \gamma_i{}^{1/2}]^2 \end{aligned}$$

Stotler and Benedict (5) empirically adjusted the interaction term $A_{o_m}$ to fit vapor-liquid equilibrium data in the system nitrogen-methane.

According to the recommended combining rule for $A_o$, the interaction term in a binary mixture should be $2x_1x_2A_{o_1}{}^{1/2}A_{o_2}{}^{1/2}$. If the coefficient of $x_1x_2$ is to be determined formally and empirically from vapor-liquid equilibrium measurements, an iterative procedure can be devised on the basis of the Newton-Raphson method. In the present study it is reasoned that the vapor-phase fugacities of hydrogen are fairly accurate, since hydrogen vapor behaves almost ideally. It was decided therefore to adjust the interaction term in the combining rule for $C_o$, for the liquid-phase hydrogen fugacity only, by a much shorter procedure. Thus in the adjustment of the combining rule for $C_o$ in the liquid phase only of a binary mixture, a direct solution for the interaction term can be obtained if one ignores the small change in $d_L$ accompanying the

TABLE 1. BENEDICT-WEBB-RUBIN EQUATION OF STATE COEFFICIENTS FOR HYDROGEN
UNITS: LB./SQ. IN. ABS., LB. MOLES/CU. FT., °*R*.

| | Eubanks (7) | Coefficients for this paper | | | |
|---|---|---|---|---|---|
| | | Set 1* | Set 2 | Set 3 | Set 4 |
| $A_o$ | 791.5 | 585.127 | ——→ | | |
| $B_o$ | 0.3782 | 0.333937 | ——→ | | |
| $C_o$ | $0.625 \times 10^6$ | $4.8282 \times 10^6$ | $2.25 \times 10^6$ | $4.41 \times 10^6$ | $4.41 \times 10^6$ |
| $a$ | 30.375 | 98.597 | ——→ | | |
| $b'$ | $0.131143 + \frac{60.75}{RT}$ | $0.08682 + \frac{197.194}{RT}$ | ——→ | | |
| $c$ | $0.55029 \times 10^6$ | $1.42317 \times 10^6$ | ——→ | | |
| $\alpha$ | 0.868577 | 0.479116 | ——→ | | |
| $\gamma$ | 0.9 | 0.9 | 0.9 | 0.74909 | † |

* From least-squares fit of Woolley *et al.*(8) hydrogen *PVT*. Mean absolute relative deviation = 0.0013%.

† $\gamma$ is a function of temperature as follows:

| $t$°, F. | $\gamma$ | $\gamma^{1/2}$ |
|---|---|---|
| 0 | 0.82810 | 0.9100 |
| −100 | 0.77440 | 0.8800 |
| −150 | 0.74909 | 0.8655 |
| −200 | 0.70057 | 0.8370 |
| −250 | 0.70057 | 0.8370 |

change in $Q$. The combining rule for $C_o$ becomes

$$C_{o_m} = x^2_1 C_{o_1} + x^2_2 C_{o_2} + Qx_1x_2$$

where $Q$ is originally $2C_{o_1}^{1/2} C_{o_2}^{1/2}$. If $\ln f^L_1$ is to equal $\ln f^G_1$ at the observed composition, then

$$Q = \frac{RT^3}{d_L\, x_2} \ln f^L_1/f^G_1 + 2C_{o_1}^{1/2} C_{o_2}^{1/2}$$

The results of adjusting the $C_o$ combining rule by the short procedure for binary mixtures indicated that a large part of the error in predicting hydrogen $K$ values could be eliminated by merely adjusting $C_o$ for pure hydrogen. Thus in the idealized combining rule for $C_o$ suggested by Benedict $Q = 2C_{o_1}^{1/2} C_{o_2}^{1/2}$, and a calculated new value of $C_o$ for hydrogen could be obtained from the above relationship. The new $C_o$ for hydrogen calculated from the values of $Q$, that is from binary *V-L* data, is shown in Table 1 as set 2. The results of the $K$ values calculated with the modified hydrogen $C_o$ indicated an improvement in the fit (by the reduction of the RMS error to 25%) but mainly in the predicted $K$ values for hydrogen in the binary mixtures. In order to improve the prediction of hydrogen $K$ in ternary mixtures, the coefficient $\gamma$ for hydrogen was adjusted; a degree of freedom was available here, namely that the least-squares fit of hydrogen *PVT* had been found to be independent of $\gamma$. However every adjustment of $\gamma$ to improve $K_{H_2}$ in ternary mixtures resulted in a poorer fit of the agreement in $K$ values in binary mixtures. An iterative trial-and-error procedure was developed whereby $\gamma$ and $C_o$ for hydrogen were adjusted alternately to arrive at the optimum combination to fit hydrogen $K$ in both binary and ternary mixtures.

### Adjusting $\gamma$ for Hydrogen

The best set of $C_o$ and $\gamma$ for hydrogen developed by the trial-and-error procedure described in the last section is

$$\begin{aligned} C_o &= 4.41 \times 10^6 \\ C_o^{1/2} &= 2.1 \times 10^3 \\ \gamma &= 0.74909 \\ \gamma^{1/2} &= 0.8655 \end{aligned}$$

These coefficients are shown as set 3 in Table 1, and the RMS error in computed $K$ values is 14%. The final value of $C_o$ does not differ greatly from the original value obtained from a least-squares fit of the hydrogen *PVT*.

Further improvements in hydrogen $K$ values were obtained by making $\gamma$ a function of temperature as shown in Table 1. The final results are listed in Table 2, and the recommended BWR coefficients for hydrogen are listed as set 4 in Table 1. The root-mean-square deviation in hydrogen $K$ values for twenty-eight runs with the recommended hydrogen coefficients is 6.6%, excluding one error of 56.2%.

TABLE 2. COMPARISON OF OBSERVED $K$ VALUES WITH THOSE CALCULATED FROM BWR EQUATION
FOR TWO AND THREE COMPONENT MIXTURES IN THE SYSTEM HYDROGEN METHANE PROPANE. DATA: (3)

| Benham and Katz run number | Liquid-phase composition parameter, $x_{C_1}/(x_{C_1} + x_{C_3})$ | Observed $K_H$ | Observed $K_{C_1}$ | Observed $K_{C_3}$ | Calculated* $K_H$ | Calculated* $K_{C_1}$ | Calculated* $K_{C_3}$ |
|---|---|---|---|---|---|---|---|
| 0°F., 500 lb./sq. in. abs. | | | | | | | |
| 46 | 0 | 39.4 | — | 0.095 | 40.6 | — | 0.094 |
| 30 | 0.119 | 34.9 | 3.70 | 0.125 | 34.5 | 3.58 | 0.119 |
| 28 | 0.163 | 30.8 | 3.76 | 0.137 | 31.8 | 3.54 | 0.131 |
| 26 | 0.238 | 25.3 | 3.40 | 0.150 | 27.6 | 3.42 | 0.146 |
| 0°F., 1,000 lb./sq. in. abs. | | | | | | | |
| 46 | 0 | 19.8 | — | 0.062 | 20.4 | — | 0.057 |
| 35 | 0.185 | 19.1 | 1.93 | 0.082 | 16.4 | 1.99 | 0.082 |
| 33 | 0.265 | 17.0 | 1.86 | 0.094 | 14.4 | 1.97 | 0.095 |
| 1 | 0.53 | — | 1.70 | 0.206 | — | 1.72 | 0.204 |
| —100°F., 500 lb./sq. in. abs. | | | | | | | |
| 46 | 0 | 63.9 | — | 0.0099 | 65.4 | — | 0.0077 |
| 18 | 0.216 | 56.3 | 1.42 | 0.0106 | 50.6 | 1.63 | 0.0107 |
| 22 | 0.437 | 36.0 | 1.75 | 0.0214 | 34.6 | 1.69 | 0.0181 |
| 20 | 0.498 | 31.8 | 1.69 | 0.0242 | 29.4 | 1.66 | 0.0211 |
| 1 | 0.62 | — | 1.59 | 0.034 | — | 1.59 | 0.0289 |
| —100°F., 1,000 lb./sq. in. abs. | | | | | | | |
| 46 | 0 | 32.8 | — | 0.0071 | 33.3 | — | 0.0050 |
| 38 | 0.354 | 18.9 | 1.07 | 0.022 | 20.4 | 1.01 | 0.012 |
| 40 | 0.606 | 11.8 | 0.909 | 0.099 | 12.0 | 1.034 | 0.024 |
| —150°F., 500 lb./sq. in. abs. | | | | | | | |
| † | 0 | 82.0 | — | 0.00198 | 82.7 | — | 0.00114 |
| 3 | 1.0 | 9.31 | 0.856 | — | 9.11 | 0.852 | — |
| —150°F., 1,000 lb./sq. in. abs. | | | | | | | |
| † | 0 | 43.6 | — | 0.00133 | 42.5 | — | 0.00082 |
| 4 | 1.0 | 4.63 | 0.651 | — | 4.45 | 0.650 | |
| —200°F., 500 lb./sq. in. abs. | | | | | | | |
| 46 | 0.086 | 121 | 0.441 | 0.0053 | 112 | 0.189 | 0.00009 |
| 44 | 0.445 | 46.6 | 0.365 | 0.0125 | 72.8 | 0.186 | 0.00012 |
| 2A | 1.0 | 18.6 | 0.374 | — | 18.8 | 0.340 | |
| —200°F., 1,000 lb./sq. in. abs. | | | | | | | |
| 45 | 0.1032 | 55.4 | 0.0365 | 0.00716 | 57.2 | 0.122 | 0.00008 |
| 43 | 0.577 | 29.2 | 0.215 | 0.00633 | 31.2 | 0.207 | 0.00012 |
| 42 | 0.595 | 29.6 | 0.208 | 0.00664 | 30.4 | 0.208 | 0.00012 |
| 41 | 0.616 | 27.8 | 0.221 | 0.00715 | 29.4 | 0.212 | 0.00013 |
| 47 | 0.863 | 13.4 | 0.241 | 0.0242 | 15.1 | 0.234 | 0.0002 |
| 5 | 1.000 | 9.74 | 0.259 | — | 9.24 | 0.246 | |
| —250°F., 490 lb./sq. in. abs. | | | | | | | |
| 12 | 1.0 | 29.1 | 0.0745 | — | 29.6 | 0.0732 | |
| —250°F., 1,490 lb./sq. in. abs. | | | | | | | |
| 13 | 1.0 | 9.98 | 0.059 | — | 9.68 | 0.061 | |

* Set 4—BWR coefficients for hydrogen; $K$ values computed at observed composition.
† Data of Williams and Katz (*4*).

### K Values for Components Other Than Hydrogen

The calculated $K$ values for methane in the final comparison of Table 2 are in reasonable agreement with observed values except for three runs. Since no trend is detectable in the deviations for methane, these discrepancies could be partly attributed to experimental error.

The agreement in propane $K$ values is a different story. The present BWR equation of state approach is still inadequate to represent propane $K$ values below —100°F. This result is not related primarily to the presence of hydrogen in the system but has been observed for all hydrocarbons heavier than methane at low temperatures, specifically for ethane and propane in the methane-ethane-propane system (9) and $n$-butane in the methane–$n$-butane system (*10*). The Lorentz combining rule for $B_{o_m}$ was explored to

Table 3. Comparison of Observed $K$ Values with Those Calculated from BWR Equation for Binary Mixtures of hydrogen ethylene and hydrogen ethane

| Temperature, °F. | Pressure, lb./sq. in. abs. | Reference | $K$ observed $H_2$ | $K$ observed $C_2$ | $K$ calculated $H_2$ | $K$ calculated $C_2$ |
|---|---|---|---|---|---|---|
| | | System hydrogen ethylene | | | | |
| 0 | 500 | (*4*) | 17.1 | 0.863 | 13.7 | 0.871 |
| 0 | 2,000 | (*4*) | 3.94 | 0.496 | 3.29 | 0.513 |
| −100 | 250 | (*4*) | 84.2 | 0.320 | 83.3 | 0.301 |
| −100 | 2,000 | (*4*) | 10.8 | 0.0924 | 10.2 | 0.0827 |
| −175 | 250 | (*4*) | 147 | 0.0408 | 162 | 0.0350 |
| −175 | 2,000 | (*4*) | 20.2 | 0.0179 | 21.8 | 0.0128 |
| | | System hydrogen ethane | | | | |
| +50 | 500 | (*4*) | 12.1 | 0.922 | 11.6 | 0.936 |
| +50 | 2,000 | (*4*) | 3.21 | 0.567 | 3.00 | 0.568 |
| 0 | 250 | (*4*) | 48.8 | 0.896 | 42.9 | 0.912 |
| 0 | 2,000 | (*4*) | 6.12 | 0.264 | 5.79 | 0.261 |
| −50 | 250 | (*4*) | 75.4 | 0.424 | 72.5 | 0.424 |
| −50 | 2,000 | (*4*) | 9.05 | 0.113 | 9.07 | 0.108 |
| −125 | 250 | (*4*) | 112 | 0.077 | 131 | 0.075 |
| −125 | 2,000 | (*4*) | 14. | 0.0246 | 17.1 | 0.022 |
| −200 | 250 | (*4*) | 160. | 0.00462 | 292. | 0.00431 |
| −200 | 2,000 | (*4*) | 23.6 | 0.00272 | 43.1 | 0.00228 |
| −121 | 302.7 | (*11*) | 91.2 | 0.088 | 105.4 | 0.0709 |
| −121 | 1171. | (*11*) | 29.8 | 0.0465 | 27.8 | 0.0284 |
| −175 | 204.3 | (*11*) | 378 | 0.0551 | 260 | 0.0157 |
| −175 | 1,137.5 | (*11*) | 76.1 | 0.0111 | 49.7 | 0.0111 |

Table 4. Comparison of Observed $K$ Values with Those Calculated from BWR Equation for Ternary Mixtures of hydrogen methane ethylene and hydrogen methane ethane

| Temperature, °F. | Pressure, lb./sq. in. abs. | | $K$ observed $H_2$ | $K$ observed $C_1$ | $K$ observed $C_2$ | $K$ calculated $H_2$ | $K$ calculated $C_1$ | $K$ calculated $C_2$ |
|---|---|---|---|---|---|---|---|---|
| | | System hydrogen methane ethylene | | | | | | |
| −121 | 441 | (*13*) | 44.3 | 1.50 | 0.115 | 42.5 | 1.39 | 0.133 |
| −121 | 1,176 | (*13*) | 9.77 | 0.674 | 0.0978 | 8.89 | 0.700 | 0.118 |
| −175 | 441 | (*13*) | 25.2 | 0.631 | 0.0306 | 30.5 | 0.591 | 0.378 |
| −175 | 1,176 | (*13*) | 25.9 | 0.438 | 0.0311 | 26.4 | 0.295 | 0.0158 |
| | | System hydrogen methane ethane | | | | | | |
| −121 | 441 | (*12*) | 162 | 1.36 | 0.0890 | 40.4 | 1.40 | 0.0750 |
| −121 | 1,176 | (*12*) | 11.8 | 0.921 | 0.0966 | 10.5 | 0.706 | 0.0648 |
| −175 | 441 | (*12*) | 24.2 | 0.638 | 0.0443 | 39.6 | 0.597 | 0.0150 |
| −175 | 1,176 | (*12*) | 12.4 | 0.352 | 0.125 | 12.3 | 0.334 | 0.0137 |
| −100 | 500 | (*19*) | 34.8 | 1.56 | 0.114 | 33.8 | 1.63 | 0.107 |
| −100 | 1,000 | (*19*) | 12.2 | 0.98 | 0.120 | 11.0 | 0.98 | 0.110 |
| −200 | 500 | (*19*) | 21.2 | 0.34 | 0.011 | 21.5 | 0.33 | 0.0072 |
| −200 | 1,000 | (*19*) | 28.8 | 0.24 | 0.0041 | 33.2 | 0.21 | 0.0032 |

assess the improvement in predicted $K$ values of propane which might result, but the effect, while large by the usual standards, did not warrant further investigation. $K$ values for propane were increased by a factor of 3 at −200°F. with the Lorentz combination for $B_o$ used, whereas a factor of several hundred is needed to match the observed values.

## COMPARISON OF PREDICTED HYDROGEN K VALUES WITH INDEPENDENT DATA

The values of the BWR coefficients for hydrogen given in Table 1 have been employed to predict the phase behavior of hydrogen in hydrogen-ethane (*4,11*) and hydrogen-ethylene (*4*) binary mixtures and hydrogen-methane-ethane (*12, 19*) and hydrogen-methane-ethylene ternary mixtures. These results are shown in Tables 3 and 4 and have been plotted in Figure 1 for the binary system hydrogen-ethylene and hydrogen-ethane at a pressure of 1,000 lb./sq.in.abs.

Generally the calculated $K$ values for hydrogen agree very well with those of Williams and Katz (*4*) except at very low temperatures, below −175°F., in the hydrogen-ethane system. It should be noted that there are marked differences in the experimental data of Williams and Katz and those of Levitskaya (*11*) on the hydrogen-ethane system at these conditions. Further, curves for the Williams and Katz experimental data on hydrogen-ethylene and hydrogen-ethane cross at −150°F., which seems to be contrary to experience, to the trends shown in the calculated $K$ values, and to the qualitative relationship demonstrated by the Levitskaya data.

While the calculated hydrogen $K$ values show serious disagreement with some of the Russian experiments, these differences are within the ±0.5 mole% accuracy claimed by Levitskaya *et al.* for their component analyses. The agreement between calculated $K$ values and the data of Cosway (*19*) is good.

## CONCLUSIONS

An empirical approach to improving the prediction of hydrogen $K$ values in mixtures with methane and propane at low temperatures has resulted in a redefinition of the Benedict-Webb-Rubin equation of state coefficient $\gamma$ as a function of temperature for hydrogen and in a small adjustment to $C_o$ for pure hydrogen.

The predicted behavior of hydrogen in binary mixtures can be markedly improved by refitting only $C_o$ in the BWR equation for hydrogen to binary *V-L* data, but in ternary mixtures such a correction to $C_o$ obtained from single-phase *PVT* is inadequate.

The predicted $K$ values for propane in mixtures with hydrogen and methane at very low temperatures ($< -150$°F.) are still too low by 2 orders of magnitude.

## NOTATION

$A_o$, $a$ = BWR equation of state coefficients
$B_o$, $b$, $b'$ = BWR equation of state coefficients
$C_o$, $c$ = BWR equation of state coefficients
$C_1$, $C_2$, $C_3$ = methane propane, ethane propane, or ethylene propane
$d_g$ = vapor-phase density, lb.-moles/cu. ft.
$d_L$ = liquid-phase density, lb.-moles/cu. ft.
$f$ = fugacity
$f^G$ = vapor-phase fugacity, lb./sq. in.
$f^L$ = liquid-phase fugacity, lb./sq. in.
$K$ = vapor-liquid equilibrium
$P$ = pressure, lb./sq. in.
$Q$ = interaction term in combining rule for equation of state coefficients

$R$ = universal gas content, (lb.) cu. ft./(sq. in.) (lb.-mole) (°R.)
$T$ = temperature, °R.
$x$ = mole fraction
$\alpha$ = BWR equation of state coefficients
$\gamma$ = BWR equation of state coefficients

**Subscripts**

$i$ = component $i$
$m$ = mixture property
1, 2 = components 1 and 2

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# The Constant-Volume Heat Capacities of Gaseous Perfluorocyclobutane and Propylene

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**The constant-volume heat capacities of gaseous perfluorocyclobutane and propylene have been measured over a considerable range of temperatures and densities with a new type of adiabatic calorimeter. This calorimeter differs from previous constant-volume gas calorimeters in having very thin walls and being equipped with an internal motor stirrer to provide temperature uniformity. The experimental results have been compared with the predictions of the Benedict-Webb-Rubin and Martin-Hou equations, by use of published values of the zero-pressure-constant-volume heat capacity. The over-all agreement is satisfactory, with a maximum difference between the experimental and calculated heat capacities of 6.7%; however the comparison reveals several interesting systematic differences between the experimental and calculated values of the derivatives of the constant-volume heat capacity with respect to temperature and density.**

Although the constant-volume heat capacity has been less intensively investigated than the constant-pressure heat capacity, it is just as useful in thermodynamic calculations as $C_p$. At zero pressure the two are related by the equation $C_v^* = C_p^* - R$. At finite pressures $C_v$ and $C_p$ may be computed from the corresponding zero-pressure values and PVT data as represented by an equation of state by use of the relations

$$C_v - C_v^* = -\int_v^\infty T\left(\frac{d^2P}{dT^2}\right)_v dV_T \qquad (1)$$

$$C_p - C_p^* = -\int_0^P T\left(\frac{d^2V}{dT^2}\right)_P dP_T \qquad (2)$$

(Although in principle the necessary second derivatives can be computed directly from PVT data, in practice such data are rarely available in such quantity and precision that the second derivatives can be calculated without recourse to a numerical equation of state or a graphical one, for example a compressibility plot.)

Comparison of the experimental values of $C_v - C_v^*$ or $C_p - C_p^*$ with those calculated by Equations (1) and (2) is a very sensitive test of the accuracy of an equation of state. Inspection of Equations (1) and (2) reveals that $C_v - C_v^*$ is readily calculated by means of a pressure-explicit equation of state, $P = f(V, T)$, and that $C_p - C_p^*$ is readily calculated by means of a volume-explicit equation $V = f(P, T)$. Computation of $C_v - C_v^*$ from a volume-explicit equation or of $C_p - C_p^*$ from a pressure-explicit equation is possible but awkward. Most currently used equations are pressure-explicit, for example the Beattie-Bridgeman (*1*), Benedict-Webb-Rubin (*2*), and Martin-Hou (*14*) equations; the accuracy of these equations can be tested and possible improvements suggested by $C_v - C_v^*$ data, but such tests cannot be conveniently made with $C_p - C_p^*$ data. Furthermore $C_p$ increases without limit near the critical state, whereas $C_v$ does not; so $C_v$ may be used to check state data near the critical point but $C_p$ may not.

The major experimental problems of $C_p$ calorimetry have long been solved (*17*); $C_v$ calorimetry presents a different set of experimental problems, which have not yet been completely overcome. Measurements of $C_p$ are performed in a flow calorimeter at steady state. As the temperature of the apparatus does not change with respect to time, the heat capacity of the calorimeter does not enter the calculations of $C_p$. Measurements of $C_v$, however, are performed in an unsteady state by heating a known mass of gas plus its container through a measured temperature interval. The heat capacity of the container must be subtracted from the measured heat capacity to compute the

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