

The general correlation of the methane partial enthalpy differences presented was compared with twelve derived methane partial enthalpy values from the methane-ethane and methane-propane binaries. The absolute average difference was 22 B.t.u./lb.-mole.

## CONCLUSIONS

The comparison of mixture enthalpy differences calculated by two equations of state with those calculated from PVTy data shows the equations of state to give fairly inaccurate values. This comparison also points out that the Benedict-Webb-Rubin equation of state should not be extrapolated into a region where coefficients for the equation have not been determined. The mixture enthalpy differences calculated from PVTy data compare reasonably well with the data of Budenholzer, et al. (4).

A general correlation for the mixture enthalpy difference of methane-light hydrocarbon binaries is presented. The correlation predicts enthalpy differences of methane binaries much better than either the Redlich-Kwong or Benedict-Webb-Rubin equations of state.

## NOTATION

$a, b, c, A, B,$  = parameters for the Redlich-Kwong equation of state and/or  
 $A_0, B_0, C_0$  = the Benedict-Webb-Rubin Equation of state  
 $H$  = enthalpy, B.t.u./lb.-mole,  $(H^P_T - H^O_T)_v + (H^O_T - H^O_0)_v$   
 $\bar{H}$  = partial enthalpy of a component, B.t.u./lb.-mole,  $(\bar{H}^P_T - H^O_T)_{v,i} + (H^O_T - H^O_0)_i$   
 $\Delta H$  = mixture enthalpy difference from an ideal gas or the effect of pressure on the mixture enthalpy, B.t.u./lb.-mole,  $(\bar{H}^P_T - H^O_T)_{v,i}$   
 $\Delta \bar{H}$  = partial enthalpy difference of a component from an ideal gas or the effect of pressure on the partial enthalpy of a component, B.t.u./lb.-mole,  $(\bar{H}^P_T - H^O_T)_{v,i}$

$H^P_T$  = enthalpy at temperature  $T$  and pressure  $P$   
 $H^O_T$  = enthalpy at temperature  $T$  and the ideal gas state  
 $H^O_0$  = enthalpy at 0 temperature and the ideal gas state  
 $\bar{H}^P_T$  = partial enthalpy at temperature  $T$  and pressure  $P$   
 $P$  = absolute pressure, lb./sq. in. abs.  
 $P^O$  = vapor pressure, lb./sq. in. abs.  
 $R$  = universal gas constant  
 $T$  = absolute temperature, °R.  
 $V$  = volume/mole  
 $y$  = mole fraction of a component in the vapor  
 $\alpha$  = residual volume, volume/mole,  $\frac{RT}{P} - V$   
 $\alpha', \gamma$  = constants for the Benedict-Webb-Rubin equation of state  
 $\omega$  = acentric factor

## Superscripts

$P$  = value at the system pressure  
 $O$  = value in the ideal gas state  
 $(0)$  = universal function of reduced temperature and pressure at  $\omega = 0$ .  
 $(1)$  = universal function of reduced temperature and pressure that is dependent on the acentric factor

## Subscripts

$0$  = zero absolute temperature  
 $1, 2$  = methane (component 1) and the heavy component (component 2) of a binary system  
 $c$  = critical values  
 $i$  = value of component  $i$   
 $pc$  = pseudo critical values  
 $pm$  = pseudo mixture values  
 $pr$  = pseudo reduced values  
 $r$  = reduced values  
 $T, P, y$  = values held constant during an operation

## LITERATURE CITED

- Benedict, Mason, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940); **10**, 747 (1942).
- , *Chem. Eng. Progr.*, **47**, 419, 449 (1951).
- Brewer, Jerome, and J. M. Geist, Paper presented at Am. Chem. Soc. Christmas Symposium, St. Louis, Missouri (December, 1960).
- Budenholzer, R. A., et al., *Ind. Eng. Chem.*, **34**, No. 7, p. 878 (1942).
- Canjar, L. N., and W. C. Edmister, *Chem. Eng. Progr. Symposium Ser.* No. 7, **49**, 73 (1953).
- Curl, R. F., and K. S. Pitzer, *Ind. Eng. Chem.*, **50**, No. 2, p. 265 (1958).
- Dodge, B. F., "Chemical Engineering Thermodynamics," pp. 235, 240, 229, McGraw-Hill, New York (1944).
- Edwards, W., E. I. Organick, and L. Larrey, IBM-650 program library, File No. 9.3.002.
- Erbar, J. H., and R. E. Thompson, Interoffice report, Oklahoma State University, Stillwater, Oklahoma (1959).
- Guggenheim, E. A., "Thermodynamics," 3 ed., p. 213, North-Holland Publishing Co., Amsterdam (1957).
- Kay, W. B., *Ind. Eng. Chem.*, **28**, 1014 (1936).
- Opfell, J. B., C. J. Pings, and B. H. Sage, Monograph on Am. Petrol. Inst. Research Project 37, Am. Petrol. Inst. (1959).
- Papadopoulos, A., R. L. Pigford, and Leo Friend, *Chem. Eng. Progr. Symposium Ser.* No. 7, **49**, 119 (1953).
- Pitzer, K. S., et al., *J. Am. Chem. Soc.*, **77**, 3433 (1955).
- Pitzer, K. S., and G. O. Hultgren, *ibid.*, **80**, Pt. 5, p. 4793 (1958).
- Prausnitz, J. M., and R. D. Gunn, *A.I.Ch.E. Journal*, **4**, No. 4, p. 430 (1958).
- Redlich, O., and J. N. S. Kwong, *Chem. Rev.*, **44**, 233 (1949).
- Rossini, F. D., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Inst. Technol., Pittsburgh, Pennsylvania (1953).
- Sage, B. H., and W. N. Lacey, Monograph on Am. Petrol. Inst. Research Project 37, Am. Petrol. Inst. (1950).
- , *Ind. Eng. Chem.*, **31**, No. 12, p. 1497 (1939).
- Sage, B. H., R. A. Budenholzer, and W. N. Lacey, *ibid.*, **32**, No. 9, p. 1262 (1940).
- Salvadori, M. G., and M. L. Baron, "Numerical Methods in Engineering," Prentice-Hall, Englewood Cliffs, New Jersey (1959).
- Yarborough, Lyman, M.S. thesis, Oklahoma State University, Stillwater, Oklahoma (May, 1961).

\* Manuscript received January 15, 1962; revision received July 23, 1962; paper accepted July 23, 1962. Paper presented at A.I.Ch.E. Denver meeting.

## ERRATA

Equation (10) of "The Heat of Solution of Gases at High Pressure," by A. E. Sherwood and J. M. Prausnitz, which appeared in the *A.I.Ch.E. Journal*, **8**, No. 4, p. 519 (September, 1962), should read

$$\ln \phi_i = -\ln z + \frac{2}{v^2} \sum_j y_j B_{ij}$$

Equation (7) of "Solubility of Chlorofluoromethanes in Nonvolatile Polar Organic Solvents," by Lyle F. Albright,

Paul T. Shannon, Francois Terrier, and Ping Lin Chueh, which appeared in the *A.I.Ch.E. Journal*, **8**, No. 5, p. 670 (November, 1962), should read

$$a_R = \frac{f^O_{RG}}{f^O_R} = \gamma_R x_R$$