Joule-Thomson and Second Virial Coefficients for Hydrocarbons

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PREVIOUS CALCULATIONS of thermodynamic properties have been based on two sources of primary data: pressure-volume-temperature measurements made under static conditions in various types of equipment and Joule-Thomson data obtained from throttling calorimeters. Joule-Thomson coefficients have been generally accepted as more reliable than low pressure *P-V-T* data, and at least one laboratory (*11*), which is the source of impressive contributions to the literature of thermodynamic properties, has used Joule-Thomson data extensively when calculating thermodynamic properties of hydrocarbons. In the past, because of a dearth of *P-V-T* data in the low pressure and low temperature regions (less than 10 atm. and 100° C.), Joule-Thomson measurements were the only source of extensive information. Recently, however, *P-V-T* information has begun to appear in the literature, and it is now possible to evaluate the reliability of Joule-Thomson work which, of necessity, has been taken more or less for granted.

A powerful consistency test for *P-V-T* data and Joule-Thomson coefficients involves second virial coefficients evaluated from the *P-V-T* data and Joule-Thomson coefficients extrapolated to zero pressure. When compressibility factors are fitted to the equation

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \tag{1}$$

the parameter B, the second virial coefficient, is a function of temperature alone. It is related to the Joule-Thomson coefficient at zero pressure through the relationship

$$(C_p\mu)_{p=0} = T^2 \frac{d(B/T)}{dT} \tag{2}$$

Until recently *P-V-T* data for hydrocarbons have been too limited to compute second virial coefficients for the same temperature range in which Joule-Thomson data were available. Hence Equation 2 had not been used as a consistency check. However, with the work of McGlashan and Potter (8), in which they determined the second virial coefficients for the six normal alkanes, propane to octane, Joule-Thomson and *P-V-T* can now be compared.

The second virial coefficients of McGlashan and Potter are in agreement with those selected by the American Petroleum Institute Research Project 44 (*1*) as the most reliable values at higher temperatures. In this region complete *P-V-T* data have been measured by various investigators. McGlashan and Potter correlated their data by

$$B/V_c = 0.145 - \frac{1.345}{T_r^2} - \frac{0.0057\,(n-1)^{3/2}}{T_r^6} \tag{3}$$

By performing the operation indicated in Equation 2 and taking zero pressure heat capacities from the API compilation (*1*), the Joule-Thomson coefficient at zero pressure can be calculated for propane, *n*-butane, and *n*-pentane. These have been plotted as dashed lines in Figure 1 and can be compared with those measured calorimetrically (*6, 7*).

A considerable difference exists which cannot be explained by uncertainties in the second virial coefficients. Furthermore, the measured Joule-Thomson coefficients appear linear instead of exhibiting curvature, as they certainly must if they obey the relationship in Equation 2. The directly measured values in Figure 1 have been obtained by extrapolation from higher pressure values and the uncertainties which follow as result of such extrapolations might account for the lack of curvature in the zero pressure values. However, these uncertainties cannot explain the wide discrepancies at low temperature.

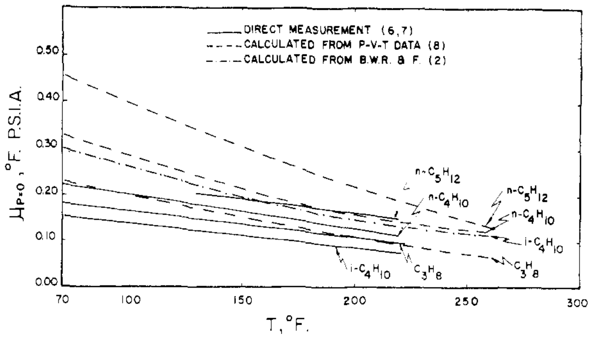

Figure 1. Joule-Thomson coefficients

Also plotted in Figure 1 are the zero pressure Joule-Thomson coefficients for isobutane (*10*). Unfortunately, *P-V-T* measurements on isobutane are not available in this temperature range. In spite of this lack, there is a suspicion that these data are inaccurate simply because of the position of the curve to the curves for propane, *n*-butane, and *n*-pentane. It is unlikely that the values for isobutane should be less than those for propane and *n*-butane. As a check, values of second virial coefficients obtained for isobutane by Benedict and others (*2*) are presented as a dashed line in Figure 1. These latter values are obtained by fitting the Benedict-Webb-Rubin equation of state to the *P-V-T* data for isobutane at higher temperatures and vapor pressure data at lower temperatures, and then using Equation 2. The Joule-Thomson coefficients calculated from the second virial coefficients fall close to the *n*-butane curve.

Since there is some question as to the reliability of the second virial coefficient as calculated by the method of Benedict and coworkers (*2*), a check was made using the Clapeyron equation. The compressibility factor at the normal boiling point and 1 atm. can be calculated from vapor pressure data, specific volume of the liquid, and heat of vaporization by means of the equation

$$Z^V = \frac{\Delta H_{vap.}}{RT^2 \dfrac{d \ln P}{dT}} + Z^L \tag{4}$$

Again using the API data (*1*) in Equation 4, a compressibility factor for isobutane vapor is found to be 0.9652 at 1 atm. and -11.73° C. compared with 0.9622 using the Benedict-Webb-Rubin equation of state. This is a stringent test of the second virial coefficient, since this temperature is far below the range in Figure 1 and for which *P-V-T* data are available.

To illustrate further the value of Equation 2 in testing Joule-Thomson coefficients, the second virial coefficient consistent with the experimental data for isobutane (*10*) has been computed and plotted in Figure 2. Also plotted is the Benedict-Webb-Rubin second virial coefficient which was obtained from high temperature *P-V-T* data and vapor pressure data and has just been shown to be consistent with the Clapeyron equation at 261.73° K. The intersection of the two curves is a mathematical necessity, because in integrating the differential Equation 2 a constant of integration must be selected. The point of intersection was arbitrarily chosen as the constant of integration. Not only do the two curves vary widely but the second virial coefficient calculated from the experimentally determined Joule-Thomson data exhibits an incorrect maximum.

Second virial coefficients consistent with the Joule-Thomson data for *n*-pentane (*7*) were similarly computed

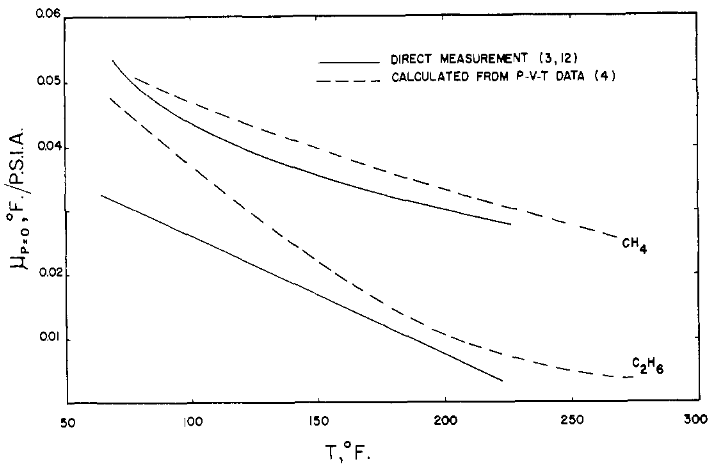

Figure 2. Second virial coefficient for isobutane

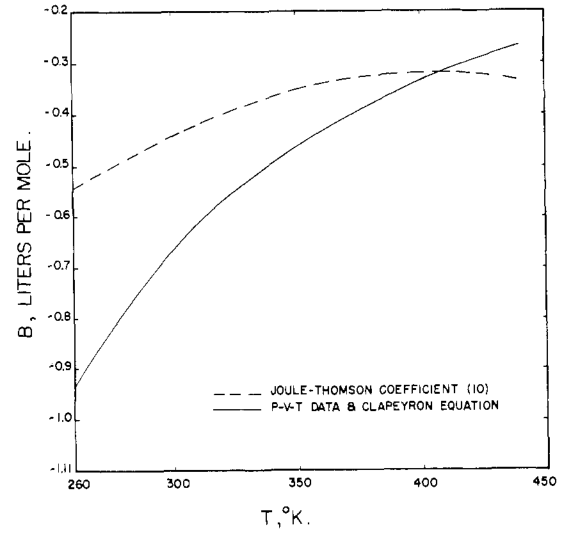

Figure 3. Joule-Thomson coefficients

and compared with those given by Equation 2. Again the values obtained from Joule-Thomson data were much higher than those derived from P-V-T data. When the integration constant was obtained using $B = -0.655$ liter per mole at 220° F., a difference of 0.2 liter per mole resulted at 100° F. (Joule-Thomson value −0.89, P-V-T value −1.1). It is unlikely that P-V-T data could be in error by this amount, as Hamann and Pearse (*5*) have obtained values of B reproducible to 0.004 liter per mole. Extraneous effects —e.g., absorption on container walls—can be detected by the differential apparatus (*5*). McGlashan and Potter, who also used this differential type apparatus, estimated the expected error to be always less than 0.040 liter per mole and in most cases less than 0.020 liter per mole.

Joule-Thomson coefficients have also been measured for methane (*3*) and ethane (*12*). These are compared with calculated values for well established P-V-T data which have been analyzed by Canjar (*4*), in Figure 3. The discrepancies are less serious here because the values of the Joule-Thomson coefficients for these compounds are relatively small in this temperature range. However, the experimentally determined values consistently fall below calculated values as in the case of the higher paraffins.

Using another type of apparatus Pattee and Brown (*9*) have determined Joule-Thomson coefficients for *n*-pentane. Their data are plotted in Figure 4 along with those of Kennedy, Sage, and Lacey (*6*) and the values calculated from P-V-T data (*1*). Oddly enough, the data fall on the high side of the calculated values, in contrast to the measurements of Kennedy, Sage, and Lacey which fall below the calculated values.

CONCLUSIONS

Contrary to previous contentions (*6, 7*), Joules-Thomson coefficients for hydrocarbons measured in the past have an uncertainty considerably greater than 1% and caution should be exercised in their use when calculating physical and thermodynamic properties. Compilations of thermodynamic properties based in part on these Joule-Thomson measurements are inaccurate in the lower temperature ranges.

NOMENCLATURE

B = second virial coefficient
C = third virial coefficient
C_p = constant pressure heat capacity
D = fourth virial coefficient
P = pressure
R = gas constant
T = temperature
T_r = reduced temperature (system temperature divided by critical temperature)

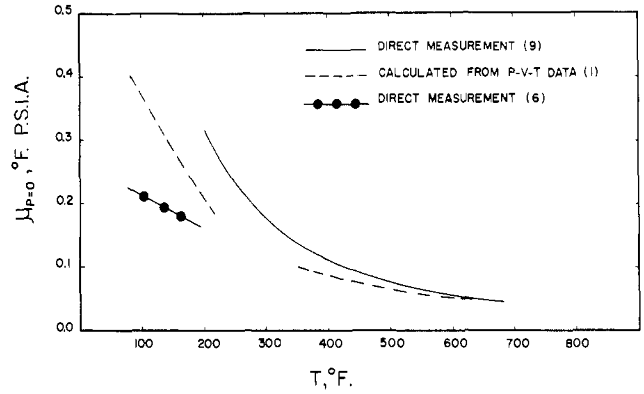

Figure 4. Joule-Thomson coefficients for *n*-pentane

V = volume
V_c = critical volume
Z = compressibility factor, PV/RT
Z^V = compressibility factor of saturated vapor
Z^L = compressibility of saturated liquid
$\Delta H_{vap.}$ = enthalpy change on vaporization (heat of vaporization)
n = number of carbon atoms in compound
μ = Joule-Thomson coefficient (rate of change of temperature with pressure at constant enthalpy)

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RECEIVED for review June 20, 1960. Accepted November 2, 1960.