13. The Joule-Thomson Inversion Curve

The Joule-Thomson coefficient, μ, is defined as the slope of an isenthalpic curve on the P-T coordinate system:

$$\mu=\left(\frac{\partial T}{\partial P}\right)_H. \tag{62}$$

Equation (62) may be rewritten for more convenient evaluation with the equation of state (39):

$$\mu=\frac{1}{C_p}\left[\frac{T}{\rho^2}\frac{\left(\frac{\partial P}{\partial T}\right)_\rho}{\left(\frac{\partial P}{\partial \rho}\right)_T}-\frac{1}{\rho}\right]. \tag{63}$$

The Joule-Thomson inversion curve is defined as the locus of points where $\mu=0$, and may be calculated from

$$\frac{T}{\rho^2}\frac{\left(\frac{\partial P}{\partial T}\right)_\rho}{\left(\frac{\partial P}{\partial \rho}\right)_T}=\frac{1}{\rho}. \tag{64}$$

In eq (64), the partial derivatives were evaluated from the equation of state (39). Equation (64) was programmed for an iterative solution to find the values of density and temperature which satisfied the equation. Pressure values were then calculated from the equation of state for the appropriate densities and temperatures.

The Joule-Thomson inversion curve data as calculated by eqs (64) and (39), are given in table 14 for 10-deg intervals.

TABLE 14. *Inversion curve from eq (64)*

Temp. K	Pressure Atm	Temp. K	Pressure Atm
130	69.27	220	431.68
140	128.64	230	454.08
150	181.92	240	473.88
160	229.83	250	491.23
170	272.96	260	506.28
180	311.83	270	519.19
190	346.81	280	530.07
200	378.27	290	539.04
210	406.48	300	546.22

Figure 20 illustrates the inversion curve and shows the comparison with other data sources. The solid line represents the locus of inversion curve points as calculated by eqs (64) and (39). The solid line is terminated at 300 K, which is the temperature limit of the data fitted by the equation of state (39). The dashed portion of the inversion curve above 300 K represents the locus of points as calculated by eq (64) with data from the equation of state which have been extrapolated beyond the fitted region.

Figure 20 also shows the inversion curve data obtained by Roebuck and Osterberg [45] in 1934. In 1940, Roebuck and Osterberg [46] published a

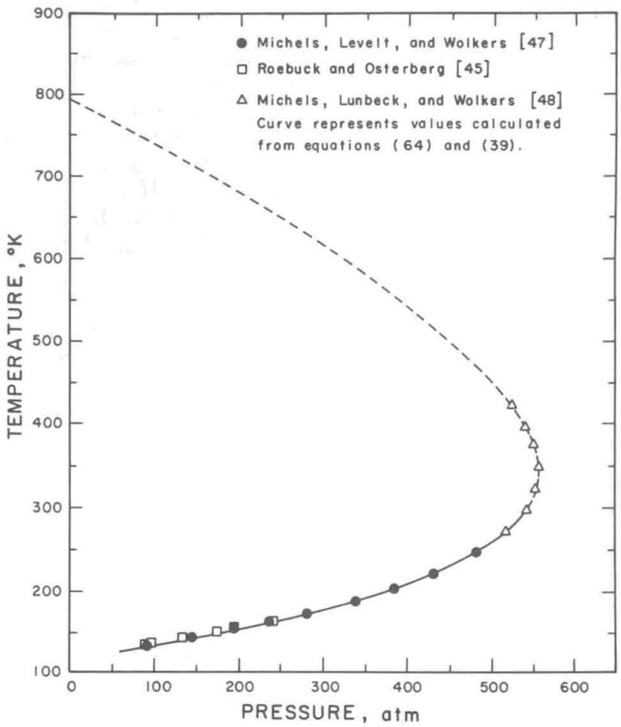

FIGURE 20. *Inversion curve comparisons.*

paper indicating that a numerical error in the pressure data had been made. Therefore, the Roebuck and Osterberg [45] data shown in figure 20 have been adjusted by the appropriate correction. The mean of the absolute values of the deviation in inversion temperatures between the corrected data of Roebuck and the values calculated by eq (64) is 1.1 percent.

Michels, Levelt, and Wolkers [47] published Joule-Thomson coefficient data for temperatures from 133 K to 273 K. From these data, the inversion curve pressures and temperatures were obtained by determining where the Joule-Thomson coefficient was equal to zero. The inversion curve data of Michels et al. [47] determined in this manner, are shown in figure 20. The mean deviation between the Michels inversion curve temperatures and the temperatures calculated by eq (64) is 0.30 percent.

Michels, Lunbeck, and Wolkers [48] published Joule-Thomson coefficient data for temperatures from 273 to 423 K. Although the equation of state was not fitted to data above 300 K, a comparison of the data of Michels and the calculated inversion curve is shown in figure 20. The mean deviation in inversion temperatures between the Michels et al. [48] data and the extrapolated values of eq (64) is 1.1 percent.

The maximum inversion temperature as calculated by eq (64) is about 794 K. Based on the Lennard-Jones 12–6 potential, Hirschfelder et al. [38] shows that the theoretical maximum reduced inversion temperature is 6.47. With this value of reduced temperature and a selected value for the ϵ/k parameter of the 12–6 potential, the theoretical maximum inversion temperature was calculated. If the value, $\epsilon/k=122$, obtained by Holborn and Otto [41] for temperatures up to 673 K is used, the theoretical maximum inversion temperature is 789 K. The deviation between the theoretical maximum inversion temperature and the value calculated by eq (64) is about 0.6 percent. If the value, $\epsilon/k=119.8$, obtained by Michels et al. [6] for temperatures up to 423 K is used, the theoretical maximum inversion temperature is 775 K, giving a deviation of about 2.5 percent. Based upon the 18–6 potential, with a value of $\epsilon/k=157.5$, the theoretical maximum inversion temperature is 770 K, giving a deviation of about 3 percent from the value calculated by eq (64).

The significance of the inversion curve as a test for the equation of state (39) may be seen by noting that the inversion curve eq (64) involves derivatives of the equation of state. As illustrated in figure 20 and as previously mentioned, the deviations between the calculated inversion curve and the data from other sources are relatively small. Therefore it may be concluded that the geometric slope of the physical thermodynamic surface is adequately described by the equation of state (39).

14. Specific Heats

The specific heats of a gas at constant pressure and constant volume are given by

$$C_v=T\left(\frac{\partial S}{\partial T}\right)_v \tag{65}$$

and

$$C_p=T\left(\frac{\partial S}{\partial T}\right)_p. \tag{66}$$

The C_p and C_v illustrated in figures 21 and 22 were calculated by forming the $\left(\frac{\partial S}{\partial T}\right)_v$ and $\left(\frac{\partial S}{\partial T}\right)_p$ numerically with $(\Delta S/\Delta T)_v$ and $(\Delta S/\Delta T)_p$, where ΔT was 0.005 K and ΔS was calculated using the equations given in section 10. These numerically obtained values were compared with values calculated from continuous analytical expressions derived

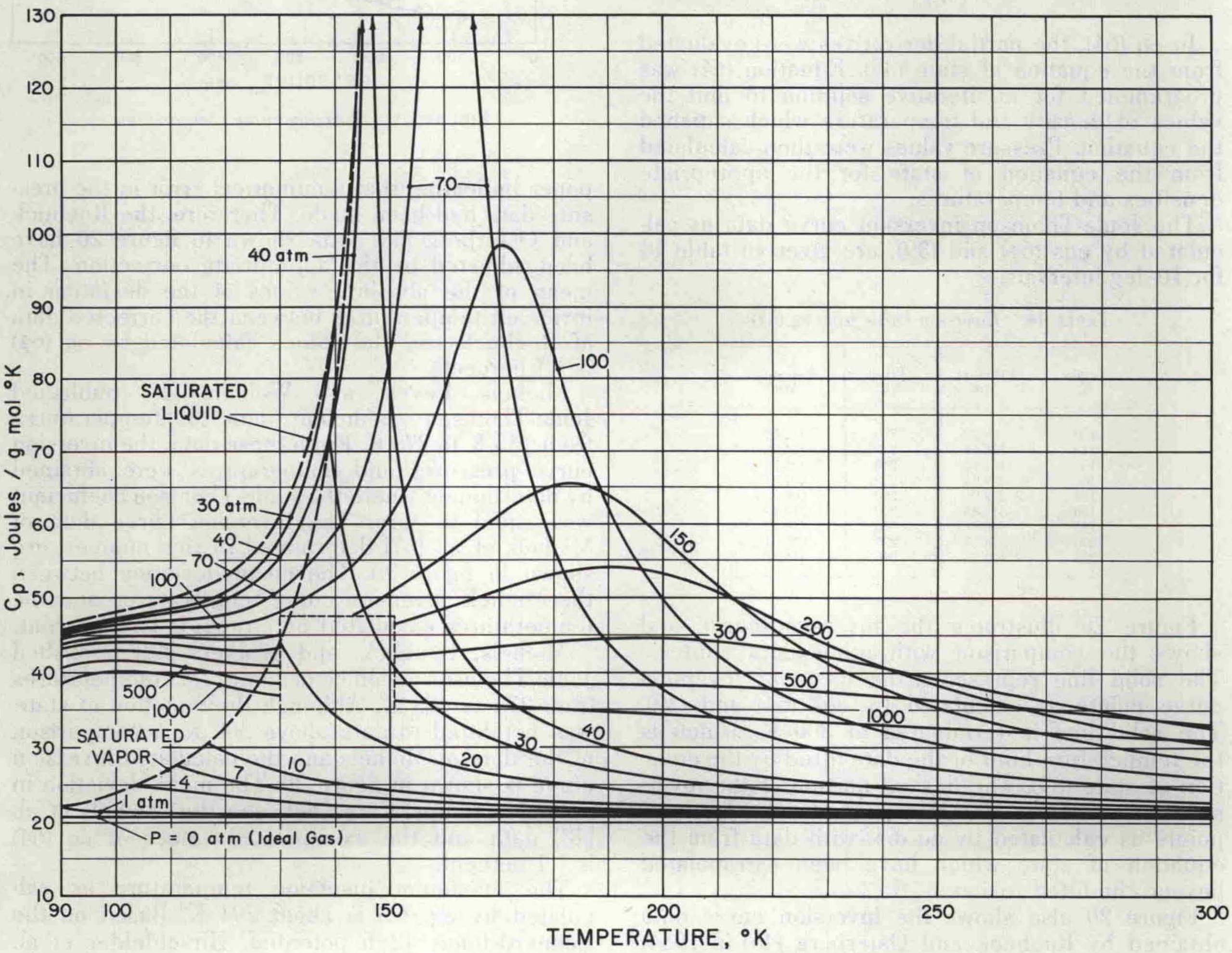

FIGURE 21. *Specific heat at constant pressure calculated by numerical method.*