Lizbeth Joy G. Tan

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Physics 151 Problem Set 5

Problem 21

Problem 2.29. Free expansion of a van der Waals gas (Gould and Tobochnik)
Calculate $(\partial T/\partial V)_E$ for the van der Waals energy equation of state (2.24) and show that a free expansion results in cooling.

Solution:
The van der Waals energy equation of state is expressed as

$$E = \frac{3}{2}NkT - N\frac{N}{V}a \tag{1}$$

For a gas in free expansion, the energy is constant so

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = 0 \tag{2}$$

From this we get

$$\left(\frac{\partial E}{\partial T}\right)_V dT = -\left(\frac{\partial E}{\partial V}\right)_T dV \tag{3}$$

For constant energy, the change in temperature with respect to volume is given by

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} \tag{4}$$

Getting the derivative on both sides of Equation (1),

$$dE = \frac{3}{2}Nk\,dT - \frac{N^2}{V^2}a\,dV \tag{5}$$

Comparing the two expressions for dE, we have

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}Nk \tag{6}$$

and

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{N^2}{V^2}a \tag{7}$$

Substituting these into Equation (4),

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{N^2a/V^2}{3/2Nk} = -\frac{2Na}{3kV^2} \tag{8}$$

Therefore the change in temperature is just the integral of this expression with respect to the volume V:

$$\Delta T = -\int_{V_1}^{V_2} \frac{2Na}{3kV^2}\,dV \tag{9}$$

and this evaluates to

$$\Delta T = \frac{2Na}{3k}\left(\frac{1}{V}\right)\Big|_{V_1}^{V_2} = \frac{2Na}{3k}\left(\frac{1}{V_2} - \frac{1}{V_1}\right) < 0 \tag{10}$$

since $V_2 > V_1$ for an expansion.