

Calculate  $\frac{P}{T} - \left(\frac{\partial P}{\partial T}\right)_V$  using the van der Waals equation of state. This is part of the free expansion problem.

The EOS is

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

where  $a$  and  $b$  are constants and

$$V = \frac{V}{\nu}$$

is the molar volume, with  $\nu =$  number of moles. We have

$$\begin{aligned}\frac{P}{T} - \left(\frac{\partial P}{\partial T}\right)_V &= \frac{P}{T} - \frac{a}{2T} \left(\frac{RT}{V-b} - \frac{a}{V^2}\right)_V \\ &= \frac{P}{T} - \frac{R}{V-b} = \frac{1}{T} \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) - \frac{R}{V-b}\end{aligned}$$

$$\boxed{\frac{P}{T} - \left(\frac{\partial P}{\partial T}\right)_V = -\frac{a}{TV^2} < 0}$$

for a van der Waals gas. Since for a free expansion we have

$$\left(\frac{\partial T}{\partial V}\right)_{\text{free exp.}} = \frac{T}{m c_V} \left[ \frac{P}{T} - \left(\frac{\partial P}{\partial T}\right)_V \right],$$

we obtain for a van der Waals gas

$$\left(\frac{\partial T}{\partial V}\right)_{\text{free exp.}} = - \frac{P}{m c_V} \frac{a}{V^2 P}$$

a

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_{\text{free exp.}} = - \frac{a}{m c_V V^2} < 0}$$

Hence the temperature of a van der Waals gas drops during free expansion.

### Reif Problem 5.12

A solid is compressed adiabatically at high pressure. We are asked to relate  $\Delta T$  to  $\Delta P$ . Hence we need to calculate  $\left(\frac{\partial T}{\partial P}\right)_S$ . This suggests

that we write  $S = S(T, P)$  and therefore

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = 0$$

to obtain

$$\left(\frac{\partial T}{\partial P}\right)_S = - \frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P}$$

Using a Maxwell relation we have

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

where  $\left(\frac{\partial V}{\partial T}\right)_P = V \alpha$

The second law yields

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial Q}{\partial T}\right)_P = \frac{m}{T} c_p$$

where  $c_p$  is the specific heat at constant pressure and  $m$  is the mass of the system.

Combining results yields

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{V \alpha}{\frac{m c_p}{T}} = \frac{T V \alpha}{m c_p}$$

For a small change in pressure and temperature, we can write

$$\Delta T = \Delta P \frac{TV\alpha}{m c_p}$$

or, in terms of the density  $\rho \equiv \frac{m}{V}$ , we have

$$\Delta T = \frac{T\alpha \Delta P}{\rho c_p}$$

### Reif Problem 5.18

For a free expansion,  $E$  is constant.

Hence the relation between  $T$  and  $V$  during a free expansion is expressed by the derivative

a)  $\left(\frac{\partial T}{\partial V}\right)_E$

This suggests that we write  $E = E(T, V)$  and then

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

which implies that

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

We can rewrite the denominator using the heat capacity at constant volume,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We also have from the first law

$$dE = T ds - P dV$$

Using this we obtain

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial s}{\partial V}\right)_T - P \left(\frac{\partial V}{\partial V}\right)_T$$

or, using Maxwell relation  $\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ ,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

Combining results yields

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_E = - \frac{\left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right]}{C_V}}$$

which is the same result obtained in class for this process (free expansion).

b) Next we calculate  $\left(\frac{\partial S}{\partial V}\right)_E$  by writing  $E = E(S, V)$  and

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV = 0$$

to obtain

$$\left(\frac{\partial S}{\partial V}\right)_E = - \frac{\left(\frac{\partial E}{\partial V}\right)_S}{\left(\frac{\partial E}{\partial S}\right)_V} = - \left( \frac{-P \cancel{\left(\frac{\partial V}{\partial S}\right)_S}}{T \cancel{\left(\frac{\partial S}{\partial V}\right)_S}} \right)$$

$$\approx \boxed{\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T}}$$

This can also be seen immediately from the first law,

$$dE = T dS - P dV$$

c) From an earlier problem, we know that

$$\left(\frac{\partial T}{\partial V}\right)_E = - \frac{a}{C_V V^2} = - \frac{a V^2}{C_V V^2}$$

for a van der Waals gas with heat capacity  $C_V$ . Integration yields

$$\int_{T_1}^{T_2} dT = \int_{V_1}^{V_2} \frac{-a V^2 dV}{C_V V^2}$$

Assuming that  $C_V = \text{constant}$ , we can carry out the integration to obtain

$$T_2 - T_1 = \frac{\alpha V^2}{C_V V} \Big|_{V_1}^{V_2}$$

or

$$T_2 - T_1 = \frac{\alpha V^2}{C_V} \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$