

PHYS 461: Midterm Exam

October 8, 2001

1 (i) We have

$$\frac{\partial c_v}{\partial v} = T \frac{\partial^2 s}{\partial v \partial T} = T \frac{\partial^2 P}{\partial T^2} = 0,$$

which shows that c_v does not depend upon v .

(ii) The differential of the molar internal energy u may be written

$$du = c_v dT + \ell dv - P dv.$$

The calorimetric coefficient ℓ is given by

$$\ell = T \left(\frac{\partial s}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v = \frac{RT}{v - b},$$

taking into account that, for a mole of a van der Waals gas,

$$P = \frac{RT}{v - b} - \frac{a}{v^2}.$$

Replacing ℓ and P by their expressions in du finally yields

$$du = c_v dT + a \frac{dv}{v^2}.$$

(iii) During a free expansion the internal energy remains constant. Writing $du = 0$ gives

$$dT = -\frac{a}{c_v} \frac{dv}{v^2}.$$

If we assume that c_v is constant in the interval $[T_f, T_i]$, we obtain

$$T_f - T_i = \frac{a}{c_v} \left(\frac{1}{v_f} - \frac{1}{v_i} \right).$$

Since $v_i < v_f$, $T_f < T_i$, and $T_f - T_i < 0$.

2 (i) The work received by the system is

$$\Delta W = - \int_{V_1}^{V_2} P dV = -P(V_2 - V_1),$$

and the heat ΔQ is, therefore, given by

$$\begin{aligned}\Delta Q &= \Delta U - \Delta W \\ &= cNR(T_2 - T_1) + P(V_2 - V_1) \\ &= cP(V_2 - V_1) + P(V_2 - V_1) \\ &= (c + 1)P(V_2 - V_1).\end{aligned}$$

Hence

$$\left| \frac{\Delta Q}{\Delta W} \right| = c + 1.$$

(ii) From the expression of the differential of the entropy

$$dS = \frac{dQ}{T} = \frac{(c + 1)P dV}{PV/NR} = N(c + 1)R \frac{dV}{V},$$

we obtain

$$S_2 - S_1 = N(c + 1)R \log \frac{V_2}{V_1}.$$

But

$$PV_2 = PV_1 - \Delta W = NRT_1 - \Delta W;$$

therefore,

$$\frac{V_2}{V_1} = \frac{PV_2}{PV_1} = 1 - \frac{\Delta W}{NRT_1},$$

and, finally,

$$S_2 - S_1 = N(c + 1)R \log \left(1 - \frac{\Delta W}{NRT_1} \right).$$