Chemistry 230 -- Quiz 5

October 10, 2001 — Tellinghuisen

Pledge and signature:

Note: If you want your paper returned folded (*i.e.*, score concealed), please print your name on the back.

1. (18) Do just **ONE** of the following two derivations (a or b): Be sure to show all steps.
   (a) Starting from $dH = TdS + VdP$, show that $(\partial H/\partial V)_T = (\alpha T - 1)/\kappa$.
   (b) Verify that $[\partial(G/T)/\partial T]_P = -H/T^2$.

(a) $dH_T = TdS_T + VdP_T \Rightarrow \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$

$dA = -SdT - PdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa}$

$\hookrightarrow \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) + V\left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha T}{\kappa} - \frac{1}{\kappa} = \frac{(\alpha T - 1)}{\kappa}$

(b) $\left(\frac{\partial (G/T)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = \frac{-TS - (H - TS)}{T^2}$

$= -H/T^2$

2. (12) We showed in one of the homework problems that, for a gas that obeys the equation of state, $PV_m = RT(1+bP)$, $(\partial U/\partial V)_T = bP^2$. Let us consider a Joule expansion for such a gas.
   (a) State the conditions on q, w, and ΔU for a Joule expansion.
   (b) Give the fundamental definition of the Joule coefficient μ_J, and then express it in terms of C_V and $(\partial U/\partial V)_T$.
   (c) Thus, obtain a differential equation in terms of dT and dV (i.e., no P dependence), which could be used to determine ΔT in a Joule expansion of a gas following the equation of state given above.
   (d) Finally, make a judicious approximation to achieve a separation of variables with all T dependence on the left-hand side and all V dependence on the right.

(a) $q = w = \Delta U = 0$

(b) $\mu_J \equiv \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$

(c) $\left(\frac{\partial T}{\partial V}\right)_U = \frac{-bP^2}{C_V} \Rightarrow C_V dT = -bP^2 dV$

$PV = nRT(1 + bP) \Rightarrow P = \frac{nRT}{V - nbRT}$

$\hookrightarrow C_V dT = -b\left[\frac{nRT}{(V - nRTb)}\right]^2 dV = -b\left[\frac{RT}{V_m - bRT}\right]^2 dV$

(d) $bRT \ll V_m \Rightarrow C_V dT \approx -\left(\frac{nRT}{V}\right)^2 b\, dV$

$C_V \frac{dT}{T^2} = -bn^2R^2\frac{dV}{V^2}$