Physics 317 assignment 9 due July 25, 2007

Carter Problems

10.2) 3rd law says $\lim_{T\to 0} \Delta S = 0$. Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

ideal gas: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$ $\therefore$ $\lim_{T\to 0}\left(\frac{\partial S}{\partial V}\right)_T \overset{3^{rd}\text{ law}}{=} 0$ but $\lim_{T\to 0} \frac{R}{V} \neq 0$

so ideal gas law cannot hold as $T \to 0$

van der Waals: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b}$ $\lim_{T\to 0}\frac{R}{v-b} \neq 0 \rightarrow$ vdW eqn not valid as $T\to 0$

10.5) (a) $C_v = bT^\alpha$ Third law $\rightarrow \lim_{T\to 0} \Delta S = 0 = \int_0^T \frac{bT^\alpha}{T} dT = \frac{bT^\alpha}{\alpha} - 0^\alpha$

Since $T^\alpha \underset{T\to 0}{\to} 0$ only for $\alpha > 0$, need $\alpha > 0$ to satisfy 3rd law

(b) $C_v = aT + bT^3$: $S - S_0 = \int_0^T \frac{C_v\, dT}{T} = \int_0^T (a + bT^2)\, dT = aT + \frac{bT^3}{3}$

10.6) $PV + f(V) = AU$ — Show $\lim_{T\to 0} C_v = 0$ for this substance

Take differential: $PdV + VdP + f'(V)dV = A\left[\underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{= C_v} dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right]$

In an isochoric process $(dV=0)$

$$VdP_v = AC_v\, dT_v \quad \text{or} \quad C_v = \frac{V}{A}\left(\frac{\partial P}{\partial T}\right)_V$$

Maxwell relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ and $\lim_{T\to 0}\left(\frac{\partial S}{\partial V}\right)_T = 0$ by 3rd law $\Rightarrow \lim_{T\to 0} C_v = 0$

10.7) Given $C = AT^{1/2} + BT^3$ for $0.05K < T < 0.5K$

$$\Delta S = \int_0^T \frac{C}{T} dT = \int_0^T (AT^{-\frac{1}{2}} + BT^2)\, dT = 2AT^{1/2} + \frac{BT^3}{3}$$

$\lim_{T\to 0} \Delta S = 0 \Rightarrow$ no violation of 3rd law; accept paper

Additional 1

$P = \frac{1}{3}u$, $U = uV$, $u = \sigma T^4$

(a) $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \infty$ since $\frac{1}{\beta} = V\left(\frac{\partial T}{\partial V}\right)_P = 0$ $(dT_P = 0)$

(b) $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \infty$ since $\frac{1}{\kappa} = -V\left(\frac{\partial P}{\partial V}\right)_T = 0$ $(dP_T = 0)$

(c) $C_V = \left(\frac{\partial U}{\partial T}\right)_V = V\left(\frac{du}{dT}\right) = 4\sigma T^3 V$

(d) C_P : $\delta Q_P = C_P \underbrace{dT_P}_{=0}$. δQ_P need not be zero $\rightarrow$ C_P is infinite

(e) No problem for limit $T \to 0$ $(\beta = 0, C_V \to 0, \Delta S \to 0 \ldots)$

Additional 2

Given $g = g_0 - s_0 T - c_V T \ln T + c_V T + RT \ln(P+a) + bP$

V_0	V_0
T_0, n	$P=0$

free expansion from V_0 to $2V_0$

Eq^n of state $v = \left(\frac{\partial g}{\partial P}\right)_T = \frac{RT}{P+a} + b \rightarrow (P+a)(v-b) = RT$

Entropy $s = s_0 + c_V \ln T + R \ln(v-b)$

Need to determine final temperature. $U = Q - W = 0$

so $dU = 0 = nc_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ $\qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = a$

$dT = \frac{-a}{nc_V}\, dV \rightarrow T_f = T_0 - \frac{a}{nc_V} V_0$

$dS = nc_V \frac{dT}{T} + nR \frac{dv}{v-b}$

$$\Delta S = n\left[c_V \ln\left(1 - \frac{aV_0}{nc_V T_0}\right) + R \ln\left(\frac{2V_0 - nb}{V_0 - nb}\right)\right]$$