

Carter Problems

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

ideal gas:  $\left(\frac{\partial P}{\partial V}\right)_T = \frac{R}{V}$   $\therefore \lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial V}\right)_T = 0$  but  $\lim_{T \rightarrow 0} \frac{R}{V} \neq 0$  <sup>3<sup>rd</sup> law</sup>

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

van der Waals:  $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b}$   $\lim_{T \rightarrow 0} \frac{R}{v-b} \neq 0 \rightarrow$  vdW eq<sup>n</sup> not valid as  $T \rightarrow 0$

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

Since  $T^d \rightarrow 0$  only for  $d > 0$ , need  $d > 0$  to satisfy 3<sup>rd</sup> law

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

10.6)  $PV + f(V) = AU$  - show  $\lim_{T \rightarrow 0} C_v = 0$  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 ( $dV=0$ )

$VdP = AC_v dT$  or  $C_v = \frac{V}{A} \left(\frac{\partial P}{\partial T}\right)_V$

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

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

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

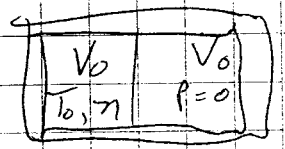
$\lim_{T \rightarrow 0} \Delta S = 0 \Rightarrow$  no violation of 3<sup>rd</sup> law; accept paper

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)  $\chi = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \infty$  since  $\frac{1}{\chi} = -V \left( \frac{\partial P}{\partial V} \right)_T = 0$  ( $dP_T = 0$ )
- (c)  $C_V = \left( \frac{\partial U}{\partial T} \right)_V = V \left( \frac{\partial u}{\partial T} \right) = 4\sigma T^3 V$
- (d)  $C_P$ :  $\delta Q_P = C_P dT_P$ .  $\delta Q_P$  need not be zero  $\rightarrow C_P$  is infinite
- (e) No problem for limit  $T \rightarrow 0$  ( $\beta \rightarrow 0$ ,  $C_V \rightarrow 0$ ,  $\Delta S \rightarrow 0 \dots$ )

Additional 2

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



Free expansion from  $V_0$  to  $2V_0$

Eq<sup>n</sup> 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  $dU = 0 = n c_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV$   $\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = a$

$dT = \frac{-a}{n c_v} dV \rightarrow T_f = T_0 - \frac{a}{n c_v} V_0$

$dS = n c_v \frac{dT}{T} + n R \frac{dV}{V-b}$

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