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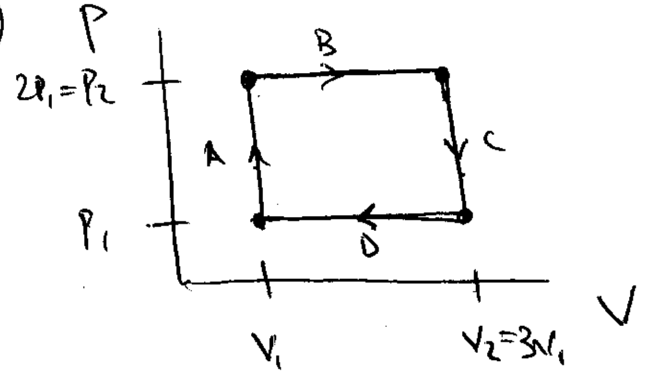
(4.1)



$$dU = TdS - pdV + \mu dN$$

$$\therefore dU = -pdV$$

$$W_A = 0 = W_C$$

{ $W > 0$ if gas does it.

$\Delta V > 0$; $p > 0$.

$\therefore \Delta W = p\Delta V$

$$W_B = +\int_{V_i}^{V_f} p\,dV$$

$$= p_B \Delta V = 2p_1 \, 2V_1 = 4p_1V_1$$

$$PV = nRT$$

$$W_D = p_D \Delta V = p_1(-2V_1) = -2p_1V_1$$

$W_T = \sum W_i$ ⇐ simply mechanical processes...

For an ideal Gas $U = U(T)$ ⇒ $\frac{\partial U}{\partial V} = 0$ i.e. does not depend at all on mechanical processes...

So $\Delta U_A = \frac{3}{2} kN \cdot \Delta T_A$

$U = N \cdot \frac{3}{2} kT$ + $PV = NkT$

$$U(P,V) = N \cdot \frac{3}{2} k \left(\frac{PV}{Nk} \right) = \frac{3}{2} PV$$

$$\Delta U = \frac{3}{2} \Delta(PV)$$

$\Delta U = Q + W_{us.}$ $\Delta U = Q - W_{gas} \rightarrow Q = \Delta U + W_{gas}$

$\Delta U_A = \frac{3}{2} V_1 \Delta P = \frac{3}{2} V_1 P_1$ ✓ $\Delta U_C = \frac{3}{2}(3V_1)(-P_1)$ ✓

$\Delta U_B = \frac{3}{2}(2P_1)(2V_1)$ ✓ $\Delta U_D = \frac{3}{2} P_1(-2V_1)$ ✓

Q > when absorbed into gas. $Q = \underline{\Delta U} + W_{gas}$

$Q_A = \frac{3}{2} V_1 P_1 + 0$
$= \frac{3}{2} V_1 P_1$

$Q_C = -\frac{9}{2} V_1 P_1 + 0 = -\frac{9}{2} V_1 P_1$

$Q_B = 6P_1V_1 + 4P_1V_1$
$= 10p_1V_1$

$Q_D = -3P_1V_1 - 2p_1V_1 = -5p_1v_1$

total heat absorbed/given off

$= \left(\frac{3}{2} + \frac{20}{2} - \frac{9}{2} - \frac{10}{2}\right) V_1 P_1 = \cancel{\frac{4}{2}P_1V_1}\ \frac{2}{2} P_1 V_1 > 0$

heat is absorbed.

total work done $= 2p_1V_1 > 0$ work is done by the gas

$\therefore$ efficiency of cycle $= \frac{W}{Q} = \frac{2p_1V_1}{p_1V_1} = 2$!!??

(b) Assume that the correct cal would have given [illegible].

cal. max/min temp when looping around cycle

then compt $1 - \frac{T_{min}}{T_{max}}$

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Prob 4.2

$T_h = 800°C$

$T_c = 20°C$

(a) $e_{max} = 1 - \frac{20}{800} = 1 - \frac{1}{25} = 1 - .04 = .96$

(b) $e'_{max} = 1 - \frac{20}{600} = 1 - \frac{1}{30} \approx 1 - .03 = \boxed{.97}$

$\frac{1}{30} > .03$

$\frac{1}{3} = .33\ldots \qquad -\frac{1}{30} < -.03$

Change in efficiency of 1%

∴ Produce 1% more energy

Assuming the plant produces 1GW (kw/hrs of power) original

it now produces an addition $10^9(.01) = 10^7$ Watts

=

of power (prob. per day)

. . .

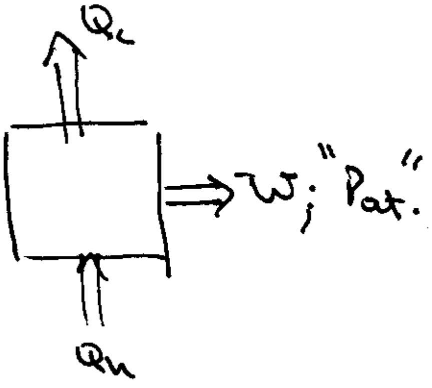
$= 4.16 \cdot 10^5$ w/hr additional + assuming there is a demand

for this addition power you make

$(4.16 \cdot 10^2 \text{ kw/hr})(.05 \text{ \$/(kw/hr)}) = \$20.8$

Prob 4.3 $P_{at.}$ ~~W~~ $= 10^9$ W.

$e = .4$



$$e \equiv \frac{W}{Q_h}$$

$$Q_h = Q_c + W.$$

(a) What is Q_c?

$$e = \frac{W}{Q_c + W} = \frac{\dot{W}}{\dot{Q}_c + \dot{W}} = \frac{1}{\frac{\dot{Q}_c}{\dot{W}} + 1}$$

$$\Rightarrow \quad \frac{\dot{Q}_c}{\dot{W}} + 1 = \frac{1}{e}$$

$$\dot{Q}_c = \dot{W}\left(\frac{1}{e} - 1\right) = (1.5)\cdot 10^9 \text{ W}.$$

(b) Plant dumps $1.5 \cdot 10^9$ W of power

$= 1.5 \cdot 10^9$ J of heat per second.

w/ a flow rate (vol/time) of 100 m^3/s

~~we have $1 m^3$ of H_2O absorbs~~ each second we have

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100 m^3 of H_2O absorbing $1.5\cdot10^9$ J of heat

$$C_p(H_2O) = 75.3\ \text{J}/\text{K}\cdot\text{mol}$$

$$V = 18.068\ \text{cm}^3/\text{mol}$$

$$C_p(H_2O) = 75.3\ \text{J}/\text{K}\cdot\text{mol}\cdot\frac{1\ \text{mole}}{18.068\ \text{cm}^3}\cdot\left(\frac{1\text{cm}}{10^{-2}\ \text{m}}\right)^3$$

$$= 4.16\cdot10^6\ \frac{\text{J}}{\text{K}\cdot\text{m}^3}$$

Thus in 1 second

$$1.5\cdot10^9\ \text{J} = (4.16\cdot10^6\ \tfrac{\text{J}}{\text{K}\cdot\text{m}^3})(100\ \text{m}^3)(T_f - 300\ \text{K})$$

$$T_f = 303.6$$

By ≈ 3.6 deg

(c) Have to dispose of $1.5\cdot10^9$ J of heat per second.

For evaporation chain amount of heat liberated would be

$$\ell = 2260\ \text{J/g} = 40.6\ \text{kJ/mol}$$

Require to know $\underset{\equiv q}{\text{m}^3/\text{s}}$ or vol flow rate of fluid

to evaporate $(1.5\cdot10^9\ \text{J/s})/\ell = q$ ___

$1\,\text{mol} = 18\,g.$

$1\,g = 1\,cm^3$

$$1\,\text{mol} = 18\,cm^3 = 18\,(10^{-2})^3\,m^3$$

$$l = 40.6\,\frac{kJ}{mol}\cdot\frac{1\,mol}{18\cdot(10^{-2})^3\,m^3} = \frac{40.6\cdot 10^3}{18}\cdot(10^6)\,J/m^3$$

$$\therefore\quad (1.5\cdot 10^9\,J/s) = q\left(\frac{40.6\cdot 10^3\cdot 10^6}{18}\,J/m^3\right)$$

$\Rightarrow$ $q = .665\,m^3/s$ required H_2O evaporation rate

The fraction this represents of the river is

$$= 6.65\cdot 10^{-3} = .6\,\%.$$

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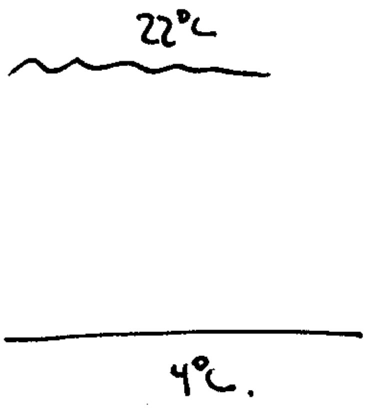
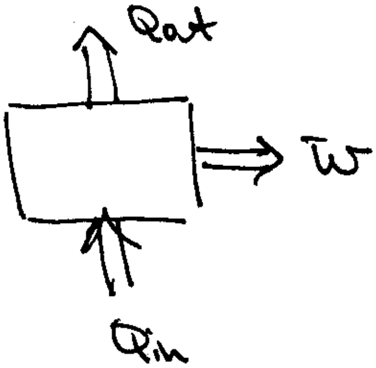
(Prob 4.4)



(a) $e_{max} = 1 - \frac{T_c}{T_h} = \cancel{1 - \frac{4}{22}} = 1 - \frac{277}{295} = .061$

(b) $\dot{W} = 10^9$ Watts



$10^9 J = ~~[illegible]~~ V c_p (T_h - T_c)$

$c_p = 4.16 \cdot 10^6 \frac{J}{K \cdot m^3}$

$10^9 J = (4.16 \cdot 10^6 \frac{J}{K \cdot m^3}) V (18)$

$V = 13.3 \ m^3$ each second ... doesn't seem unreasonable ...

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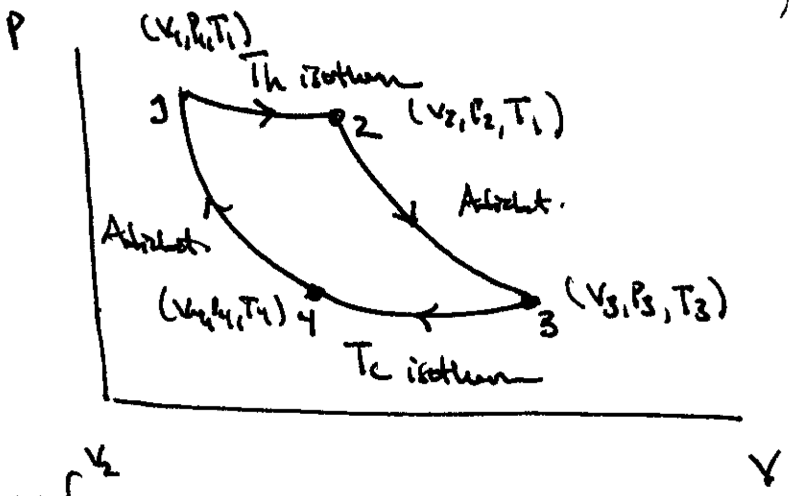
Prob 4.5

$PV = NkT$

$U = N \cdot f \cdot \frac{1}{2}kT$

$= N \frac{f}{2}kT$



1→2:

$$W_{12} = \int_{V_1}^{V_2} P\,dV = NkT \int_{V_1}^{V_2} \frac{dV}{V} = NkT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U_{12} = N \frac{f}{2} k\, \Delta T_{12} = 0 \quad \text{since } T_1 = T_2$$

$$Q_h = \Delta U + W = W = NkT \ln\left(\frac{V_2}{V_1}\right) > 0 \Rightarrow \text{heat absorbed}$$

2→3:

For an Adiabatic process $\bar{d}Q = 0$.

$$dU = \cancelto{0}{\bar{d}Q} - \bar{d}W = -p\,dV$$

$$\parallel$$

$$\cancel{N} \frac{f}{2} \cancel{k}\, dT = - \frac{\cancel{N}\cancel{k}T}{V} dV$$

$$\frac{f}{2} \frac{dT}{T} = - \frac{dV}{V} \Rightarrow V^{\gamma} p = \text{const.} \Rightarrow p = qV^{-\gamma} = \frac{P_2 V_2^{\gamma}}{V^{\gamma}}$$

$$\gamma = \left(\frac{f+2}{f}\right)$$

$$W_{23} = \int_2^3 p\,dV = \int_2^3 qV^{-\gamma}\,dV$$

$$W_{23} = \frac{C_1 V^{-r+1}}{-r+1}\Big|_2^3$$

$$= \cancel{\frac{C_1}{1-r}\left(\frac{1}{V^{1-r}}\right)}\Big|_2^3 = \frac{C_1}{1-r}$$

$$= \frac{C_1}{1-r} V^{1-r}\Big|_2^3 = \frac{C_1}{1-r}\left(V_3^{1-r} - V_2^{1-r}\right)$$

$$= \frac{P_2 V_2^{r}}{1-r}\left(V_3^{1-r} - V_2^{1-r}\right)$$

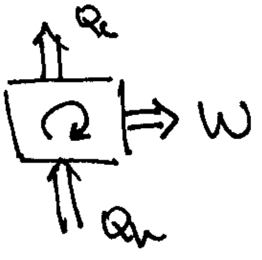
$$= \frac{1}{1-r}\left(P_3 V_3^{r} \cdot V_3^{1-r} - P_2 V_2\right)$$

$$= \frac{1}{1-r}\left(P_3 V_3 - P_2 V_2\right) \qquad PV = NkT$$

$$= \frac{1}{1-r}\left(NkT_3 - NkT_2\right) = \frac{Nk}{1-r}(T_3 - T_2) = \frac{Nk}{1-r}(T_3 - T_1)$$

- - - -

$$e = \frac{W}{Q_h} \equiv 1 - \frac{Q_c}{Q_h}$$



$$W = Q_h - Q_c$$

Since the Q_h comes from the T_h isotherm

+ the Q_c comes from the T_c isotherm

$$Q_h = NkT_h \ln\left(\frac{V_2}{V_1}\right)$$

Along path 3→4 the same arguments hold +

$$W_{34} = NkT_c \ln\left(\frac{V_4}{V_3}\right) = Q_c$$

→ > 0 ⇒ heat absorbed ... want it to be positive to represent heat expelled.

~~Then~~ ~~[illegible]~~ ~~expos.~~ ∴ $Q_c = NkT_c \ln\left(\frac{V_3}{V_4}\right)$

$$\therefore \quad e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}\frac{\ln\left(\frac{V_4}{V_3}\right)}{\ln\left(\frac{V_2}{V_1}\right)}$$ ✓

express $\frac{V_4}{V_3}$ in terms of V_2 + V_1's. + T_h + T_c

along an adiabat. (i) $PV^{\gamma} = P_0V_0^{\gamma}$ (ii) $VT^{f/2} = V_0T_0^{f/2}$

for an ideal gas $\left\{\gamma = \frac{f+2}{f}\right\}$ ∴ $\frac{V}{V_0} = \left(\frac{T_0}{T}\right)^{f/2}$.

∴ $\cancel{\frac{V_4}{V_1} = \left(\frac{T_h}{T_c}\right)^{f/2}}$ + $\cancel{\frac{V_2}{V_1} = f}$

$$\frac{V_4}{V_1} = \left(\frac{T_h}{T_c}\right)^{f/2} \qquad \frac{V_3}{V_2} = \left(\frac{T_h}{T_c}\right)^{f/2}$$

Thus: $V_4 = V_1 \left(\frac{T_h}{T_c} \right)^{f/2}$

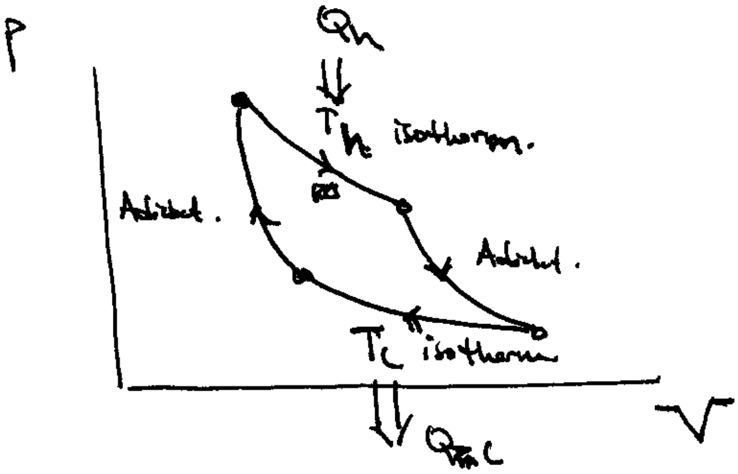
$V_3 = V_2 \left(\frac{T_h}{T_c} \right)^{f/2}$

$$\therefore \frac{\ln\left(\frac{V_4}{V_3}\right)}{\left[-\ln\left(\frac{V_2}{V_1}\right)\right]} = \frac{\ln\left(\frac{V_1 \left(\frac{T_h}{T_c}\right)^{f/2}}{V_2 \left(T_h/T_c\right)^{f/2}} \right)}{\left[-\ln\left(\frac{V_2}{V_1}\right)\right]} = +1$$

$$\therefore \quad e = 1 - \frac{T_c}{T_h}$$

Prob 4.6

(a)



$$Q_h = NkT \ln\left(\frac{V_f}{V_i}\right)$$

Assume an amount of heat Q_h flows into the cycle.

$$\Delta S_{\text{isotherm 1}} = -\frac{Q_h}{T_h} + \frac{Q_h}{T_{hw}}$$

$$\Delta S_{\text{isotherm 2}} = -\frac{Q_c}{T_{cw}} + \frac{Q_c}{T_c}$$

$$\Delta S_{\text{total}} \geq 0$$

$$\Rightarrow \quad -\frac{Q_h}{T_h} + \frac{Q_h}{T_{hw}} - \frac{Q_c}{T_{cw}} + \frac{Q_c}{T_c} \geq 0$$

$$Q_h\left(\frac{1}{T_{hw}} - \frac{1}{T_h}\right) + Q_c\left(\frac{1}{T_c} - \frac{1}{T_{cw}}\right) \geq 0$$

Since the process is cyclical $\Delta S_{\text{total}} \equiv 0$ $\therefore$ equality in the above holds.

(b) $W = Q_h - Q_c$

$$\dot{W} = \dot{Q}_h - \dot{Q}_c$$

$$\Rightarrow \quad P = k(T_h - T_{hw}) - k(T_{cw} - T_c)$$

Eliminating T_{cw} from pt (a) gives,

$$\frac{Q_h}{Q_c}\left(\frac{1}{T_{hw}} - \frac{1}{T_h}\right) + \frac{1}{T_c} = \frac{1}{T_{cw}}$$

$$\Rightarrow \quad T_{cw} = \frac{1}{\frac{Q_h}{Q_c}\left(\frac{1}{T_{hw}} - \frac{1}{T_h}\right) + \frac{1}{T_c}}$$

$\therefore$ ~~$P = k(T_h - T_{hw}) - \frac{k}{\qquad}$~~

$$\Rightarrow \quad P(T_{hw}) = k(T_h - T_{hw}) - k\left[\frac{1}{\frac{Q_h}{Q_c}\left(\frac{1}{T_{hw}} - \frac{1}{T_h}\right) + \frac{1}{T_c}} - T_c\right]$$

(c) $$P'(T_{hw}) = -k - k\left[\frac{1}{\left(\frac{Q_h}{Q_c}\left(\frac{1}{T_{hw}} - \frac{1}{T_h}\right) + \frac{1}{T_c}\right)^2} \cdot \left(\frac{Q_h}{Q_c}\right)\left(\frac{-1}{T_{hw}^2}\right)\right] \overset{set}{=} 0$$

$$+1 = +\frac{\left(\frac{Q_h}{Q_c}\right)\left(\frac{1}{T_{hw}}\right)^2}{\left(\qquad\qquad\right)^2}$$

$$\left(\frac{Q_h}{Q_c}\right)^2\left(\frac{1}{T_{hw}}-\frac{1}{T_h}\right)^2+\frac{2}{T_c}\left(\frac{Q_h}{Q_c}\right)\left(\frac{1}{T_{hw}}-\frac{1}{T_h}\right)+\frac{1}{T_c^2}=\left(\frac{Q_h}{Q_c}\right)\left(\frac{1}{T_{hw}}\right)^2$$

$$\Rightarrow \left(\frac{Q_h}{Q_c}\right)^2\left[\frac{1}{T_{hw}^2}-\frac{2}{T_{hw}T_h}+\frac{1}{T_h^2}\right]$$

(d) $e = 1 - \sqrt{\frac{T_c}{T_h}}$

$$e = 1 - \sqrt{\frac{273+25}{273+600}} = .415$$

~~$e_{const} = 1 - \sqrt{\;}$~~

$$e_{const} = 1 - \frac{273+25}{273+600} = .65$$

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Prob 4.7 Because you need a place to dump the Qh heat. Dumping it in the middle of the room would be counter productive

Prob 4.8 No. Most internal refrigerators take heat from the internal compartment & put it ~~the~~ ~~the~~ into the room. & with the door open the heat ~~would~~ removed would/could find its way back into the fridge creating an ∞ cycle

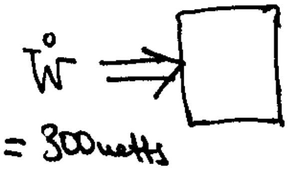
Prob 4.9

$$COP \leq \frac{T_c}{T_h - T_c} = \frac{1}{\frac{T_h}{T_c} - 1} = \frac{1}{\frac{298}{293} - 1} = 58.9$$

$T_c \cong 273 + 20 = 293$

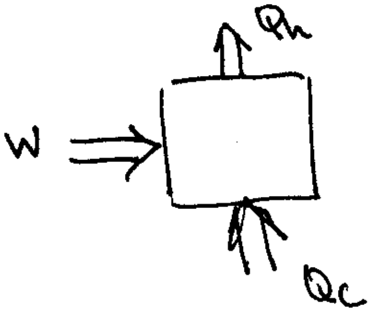
$T_h \cong 273 + 25 = 298$

Prob 4.10



Then it must expell ~~heat~~ 300 watts of heat at Tc to Th

Energy-flow diagram



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Thus the heat flowing in should be

$\dot{Q}_c$ so an energy system would be

✓

$$\dot{Q}_h = \dot{Q}_c + \dot{W}$$

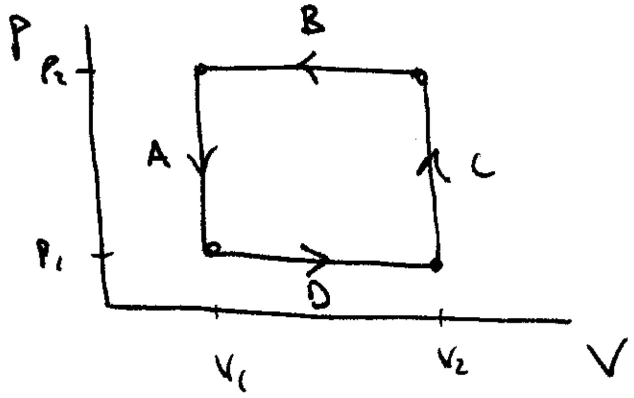
Not sure how to solve . . .

Prob 4.11

$$COP \leq \frac{T_c}{T_h - T_c} = \frac{1}{\frac{T_h}{T_c} - 1}$$

$$COP \leq \frac{1}{\frac{1}{.01} - 1} = \frac{1}{99} = 1.01 \cdot 10^{-2}$$

Prob 4.12



$$\Delta S = 0.$$

ΔW = Area under cyclic graph [illegible] [illegible]

$$= (V_2 - V_1)(P_2 - P_1)$$

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[illegible]: [illegible]: $U = N\cdot\frac{f}{2}kT$; $PV = NkT$

path A: $\Delta U = Q - W.$

$$W_A = \int p\,dV = 0$$

$$\Delta U_A = N\cdot\frac{f}{2}k\Delta T = N\frac{f}{2}k\left(\frac{P_1V_1}{Nk} - \frac{P_2V_2}{Nk}\right)$$

$$= \frac{f}{2}(P_1V_1 - P_2V_2)$$

$$Q_A = \Delta U + W = \frac{f}{2}(P_1V_1 - P_2V_2) = \frac{fV_1}{2}(P_1 - P_2) < 0$$

path B: path D:

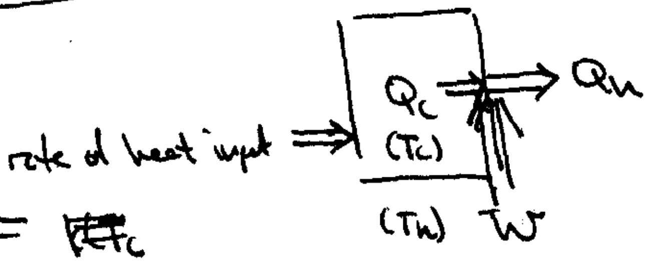
⋮

Since this is a cyclic path $\Delta U_{ADCB} = 0$

$$\therefore \quad W = Q$$

I don't see why this won't work as an engine except one pumps as much heat as [illegible] work that one puts in...

Prob 4.13



= ~~kT~~c

$$k(T_h - T_c) = \dot{Q}_{in}$$

to obtain a steady state situation the energy balance would be

$$\dot{Q}_{in} = \dot{Q}_c \qquad Q_h = \underline{W} + Q_c$$

$$\dot{Q}_h = \dot{W} + \dot{Q}_c$$

$$= \dot{W} + k(T_h - T_c)$$

$$\dot{W} = \dot{Q}_h - k(T_h - T_c)$$

... How do?

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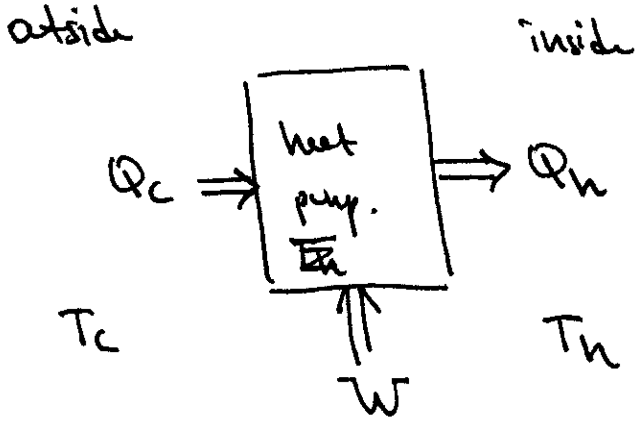
Prob 4.14



(a) $COP = \frac{Q_h}{W}$ because this ratio represents the benefit amount of heat pumped into the room ÷ amount of work required to obtain this

(b) energy cons requires

$W + Q_c = Q_h$

$1 + \frac{Q_c}{W} = \frac{Q_h}{W} = COP$ $COP \geq 1$ yes.

(c) ~~By~~ usage ~~the entropy input~~ increase ~~at Tc is~~

$\frac{Q_c}{T_c}$ ~~+ entropy decrease is~~ $\frac{Q_h}{T_h}$

~~$\Delta S \geq 0$ requires~~ + $\frac{Q_c}{T_c}$ = entropy lost by environment.

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$\frac{Q_h}{T_h}$ = entropy gained by room

$$\Delta S = -\frac{Q_c}{T_c} + \frac{Q_h}{T_h} \geqslant 0$$

$$\frac{Q_h}{T_h} \geqslant \frac{Q_c}{T_c} \quad \dotplus \quad \boxed{\frac{Q_h}{Q_c} \geqslant \frac{T_h}{T_c}}$$

$$\therefore \quad \underset{?}{\underset{\|}{\frac{W}{Q_c}}} + 1 = \frac{Q_h}{Q_c} \geqslant \frac{T_h}{T_c}$$

since

$$1 + \frac{Q_c}{W} = \frac{Q_h}{W}$$

$$\cancel{\frac{Q_c}{W} = \frac{Q_h}{W} - 1}$$

$$\cancel{\frac{W}{Q_c} = \frac{1}{\frac{Q_h}{W} - 1}} \quad \star$$

$$\therefore \quad \frac{1}{\frac{Q_h}{W} - 1} + \frac{\frac{Q_h}{W} - 1}{\frac{Q_h}{W} - 1} \geqslant \frac{T_h}{T_c}$$

$$\frac{Q_h}{W} \qquad \ldots$$

$$\cancel{\frac{\frac{Q_h}{W}}{\frac{Q_h}{W}-1}} \geq \frac{T_h}{T_c}$$

Since

$$COP = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c} = \frac{\frac{Q_h}{Q_c}}{\frac{Q_h}{Q_c}-1}$$

$$= 1 + \frac{1}{\frac{Q_h}{Q_c}-1} \leq 1 + \frac{1}{\frac{T_h}{T_c}-1}$$

$$\therefore \quad COP \leq \frac{\frac{T_h}{T_c}-1+1}{\frac{T_h}{T_c}-1} = \frac{\frac{T_h}{T_c}}{\frac{T_h}{T_c}-1} \cdot \frac{T_c}{T_c}$$

$$COP \leq \frac{T_h}{T_h - T_c}$$

(d) $T_h = 20°C = 293\,K$

$T_c =$ ~~10°C~~ $0°C = 273\,K$ $\quad COP \leq 14.65.$

$$COP = \frac{Q_h}{W}.$$

converting electrical work into (directly) into heat results in a COP = 1 where one can see from above values greater than 1 are easily obtained.

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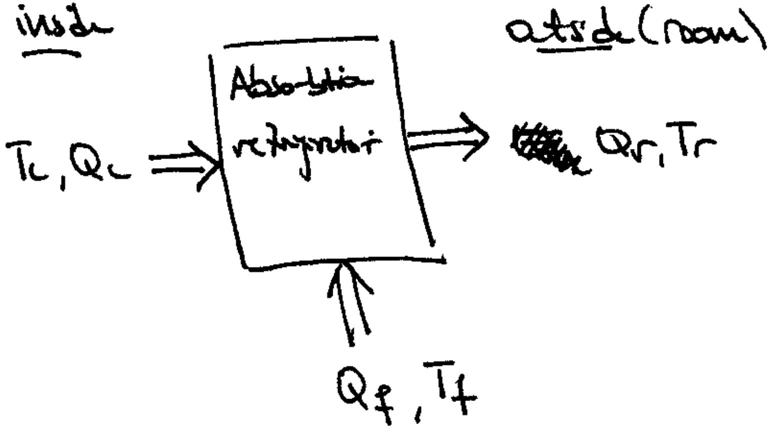
Prob 4.15



(a) $cop \equiv \frac{Q_c}{Q_f}$ this is the classic benefit/cost ratio.

(b) $Q_r = Q_c + Q_f$

$\frac{Q_r}{Q_f} = \frac{Q_c}{Q_f} + 1 \Rightarrow \frac{Q_c}{Q_f} = \frac{Q_r}{Q_f} - 1 \overset{?}{\geq} 1$

$Q_r \geq 2Q_f$ ... don't know

how to tell if this is possible ...

(c) ~~By~~ entropy ~~[illegible]~~

$$\Delta S = -\frac{Q_c}{T_c} - \frac{Q_f}{T_f} + \frac{Q_r}{T_r} \geq 0.$$

$$-\frac{1}{T_c}\frac{Q_c}{Q_f} - \frac{1}{T_f} + \frac{Q_r}{Q_f}\cdot\frac{1}{T_r} \geq 0$$

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$$-\frac{1}{T_c}\frac{Q_c}{Q_f} - \frac{1}{T_f} + \frac{1}{T_r}\left(\frac{Q_c}{Q_f}+1\right) \geq 0$$

$$\left(-\frac{1}{T_c}+\frac{1}{T_r}\right)\frac{Q_c}{Q_f} - \frac{1}{T_f} + \frac{1}{T_r} \geq 0$$

$$\left(\frac{-T_r+T_c}{T_rT_c}\right)\frac{Q_c}{Q_f} \geq \frac{1}{T_f}-\frac{1}{T_r}$$

$$\cancel{\left(\frac{T_c-T_r}{T_rT_c}\right)}$$

$$-\frac{(T_r-T_c)}{T_rT_c}\frac{Q_c}{Q_f} \geq \frac{T_r-T_f}{T_f\cdot T_r} = -\frac{(T_f-T_r)}{T_f\cdot T_r}$$

$$\frac{Q_c}{Q_f} \leq \frac{\cancel{T_r}T_c}{(T_r-T_c)}\frac{(T_f-T_r)}{T_f\cdot \cancel{T_r}} = T_c\frac{(T_f-T_r)}{(T_r-T_c)}$$

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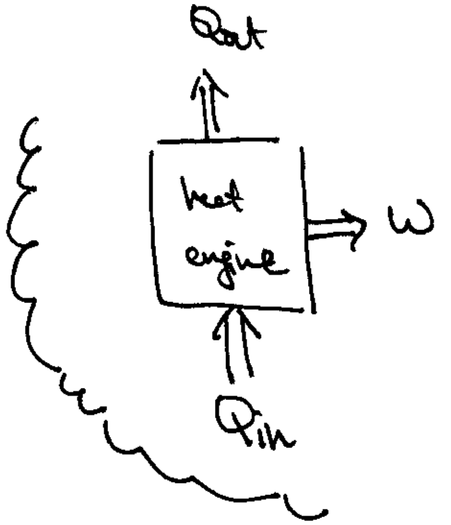
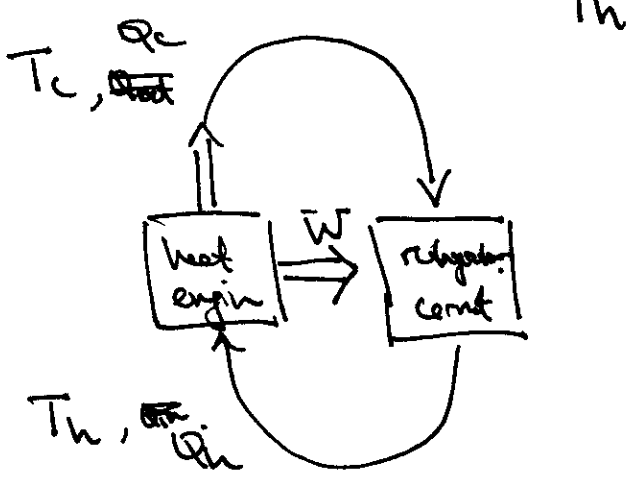
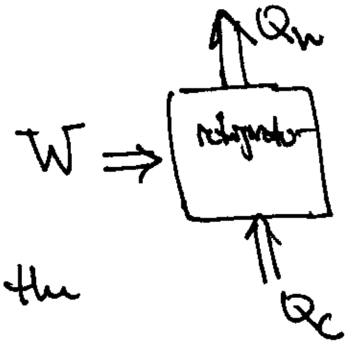
Prob 4.16

$$e_{carnot} = 1 - \frac{T_c}{T_h}$$



Assume $e_{wex} \geq 1 - \frac{T_c}{T_h}$





Thus we use the heat engine to drive the refrigerator.

Lets check that the energy's add up.

heat engine : $Q_h = Q_c + W$

refrig : $Q_c + W = Q_h$ ✓.

~~Entropy~~ $e_{carnot} = 1 - \frac{T_c}{T_h}$

Entropys add up :

$\frac{Q_c}{T_c}$ $\frac{Q_h}{T_h}$

looks like $\Delta S = 0$.

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Check that no work is req

$$\frac{W}{Q_h} \equiv e_{\text{heating}} \cancel{\geq} > 1 - \frac{T_c}{T_h}$$

$$e_{\text{refrig}} \equiv \frac{Q_c}{W}$$

$$W > e_{\text{heat}} \cdot Q_h$$

$$e_{\text{refrig}} > \frac{Q_c}{e_{\text{heat}} Q_h} \quad \ldots$$

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Prob 4.17 Hook the systems as shown in problem 4.16.

But I can not see how to show the analytic statement . . .

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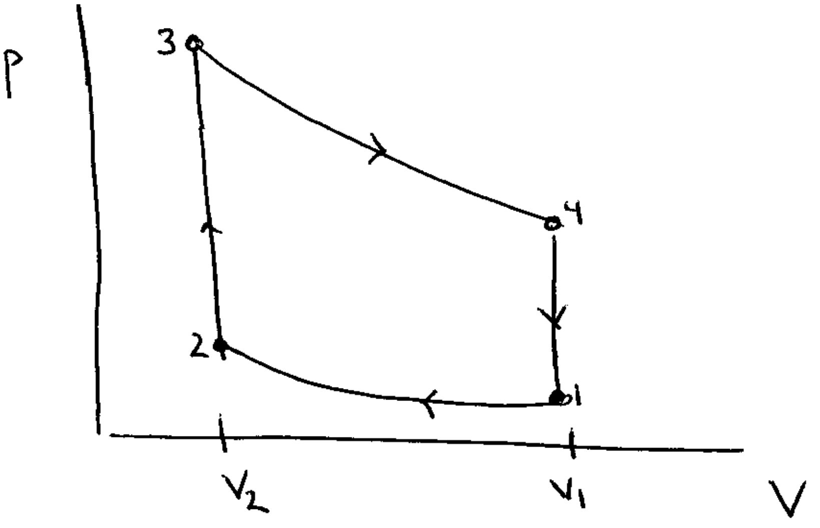
Prob 4.18

Pv: $e = 1 - \left(\frac{V_2}{V_1}\right)^{r-1}$ For the otto cycle



$PV^r = $ const

$e = \frac{W}{Q_h}$

Work done by the gas on the expansion portion of the curve 3 → 4.

$$W = \int_3^4 P\,dV = C\int_3^4 V^{-r}\,dV = C\left.\frac{V^{-r+1}}{1-r}\right|_3^4 = \frac{C}{1-r}\left(V_4^{1-r} - V_3^{1-r}\right)$$

$r > 1$ $W_{34} > 0$ ✓

$$W_{34} = \frac{1}{1-r}\left(P_4V_4^{r}\cdot V_4^{1-r} - P_3V_3^{r}V_3^{1-r}\right) = \frac{1}{1-r}\left(P_4V_4 - P_3V_3\right)$$

Work done on the compression part of the cycle 1→2

$$W = \int_1^2 P\,dV = \frac{C}{1-r}\left(V_2^{1-r} - V_1^{1-r}\right)$$

$$= \frac{-C}{r-1}\left(\frac{1}{V_2^{1-r}} - \frac{1}{V_1^{1-r}}\right) < 0. ✓$$

$$= \cancel{\frac{1}{r-1}}\left(\cancel{P_2V_2} - \right.$$

$V_2 < V_1$

$V_2^{1-r} < V_1^{1-r}$

$\frac{1}{V_1^{1-r}} < \frac{1}{V_2^{1-r}}$

$$W_{12} = \frac{1}{1-\gamma}(P_2V_2 - P_1V_1)$$

$$\therefore W_{total} = \frac{1}{1-\gamma}\left[P_4V_4 - P_3V_3 + P_2V_2 - P_1V_1\right]$$

Q_h = heat brought in

$+ \quad \Delta U = Q_h + - \cancel{W}^{0}$

$\quad\quad \|$

$\frac{f}{2}Nk\Delta T = Q_h$

$$N\frac{f}{2}k\left[{}^{P}T_3 - T_2\right] = \frac{N\cdot f\cdot k}{2}\left[\frac{P_3V_3}{Nk} - \frac{P_2V_2}{Nk}\right]$$

$$= \frac{f}{2}(P_3V_3 - P_2V_2) = Q_h$$

Now $\gamma = \frac{f+2}{f}$

$\Rightarrow \gamma f - f = 2$

$(\gamma-1)f = 2$

$f = \frac{2}{\gamma-1} \quad \therefore \quad Q_h = \frac{1}{\gamma-1}(P_3V_3 - P_2V_2)$

Now

$$e = \frac{W}{Q_h} = \frac{\frac{1}{1-\gamma}(P_4V_4 - P_3V_3 + P_2V_2 - P_1V_1)}{\frac{1}{\gamma-1}(P_3V_3 - P_2V_2)}$$

$$e = \frac{-\left(P_4V_4 - P_3V_3 + P_2V_2 - P_1V_1\right)}{P_3V_3 - P_2V_2}$$

$$= 1 - \frac{\left(P_4V_4 - P_1V_1\right)}{P_3V_3 - P_2V_2}$$

Now $P_4V_4^{r} = P_3V_3^{r}$

$$\left.\begin{matrix} 1 \leftrightarrow 2 \\ 3 \leftrightarrow 4 \end{matrix}\right\} \Rightarrow \begin{matrix} 1 \leftrightarrow 4 \\ 2 \leftrightarrow 3 \end{matrix} \; ?$$

$$P_4V_4 = \frac{P_3V_3^{r}}{V_4^{r-1}}$$

$$= \frac{P_3V_2^{r}}{V_1^{r-1}}$$

$$e = 1 - \frac{P_4V_1 - P_1V_1}{P_3V_2 - P_2V_2} = 1 - \left(\frac{V_1}{V_2}\right)\left(\frac{P_4 - P_1}{P_3 - P_2}\right)$$

$$P_4 = \left(\frac{P_3V_3^{r}}{V_4^{r}}\right) = P_3\left(\frac{V_2}{V_1}\right)^{r}$$

$$e = 1 - \left(\frac{V_1}{V_2}\right)\left[\frac{P_3\left(\frac{V_2}{V_1}\right)^{r} - P_1}{P_3 - P_2}\right] = 1 - \left(\frac{V_1}{V_2}\right)\left[\frac{P_3\left(\frac{V_2}{V_1}\right)^{r} - P_1}{P_3 - P_1\left(\frac{V_1}{V_2}\right)^{r}}\right]$$

$$P_2 = \frac{P_1V_1^{r}}{V_2^{r}}$$

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$$e = 1 - \left(\frac{V_1}{V_2}\right)\left[\cancelto{1}{\frac{P_3\left(\frac{V_2}{V_1}\right)^r - P_1}{P_3\left(\frac{V_2}{V_1}\right)^r - P_1}}\right]\frac{\left(\frac{V_2}{V_1}\right)^r}{1}$$

$$e = 1 - \frac{V_1}{V_2}\cdot\left(\frac{V_2}{V_1}\right)^r$$

$$= 1 - \left(\frac{V_2}{V_1}\right)^{r-1}$$ eq 4.10.

Prob 4.19

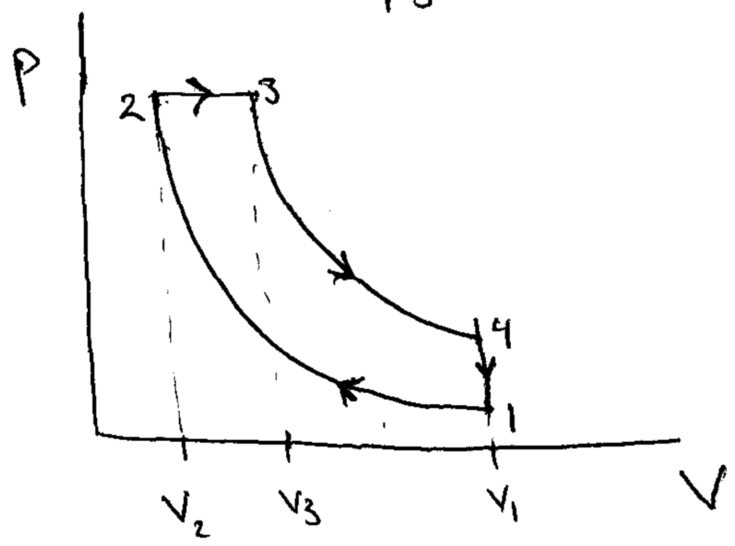
$$e = \frac{W}{Q_h}$$

For very large compression ratios the amount of time the piston spends sliding increases. Thus the influence of friction is more.

I would expect the engine to be most efficient when operating at low power by analogy w/ the Carnot engine which operates very slowly.

I don't understand why/how one can burn more fuel & increase the power but the efficiency does not change.

Prob 4.20



$e = ? = e\left(\frac{V_1}{V_2}, \frac{V_3}{V_2}\right)$

For the ~~[illegible]~~ diesel engine the heat flows into the engine during 2→3

~~[illegible]~~

The work done during the entire cycle = area

$$W_{23} = \int_2^3 p\,dV = p(V_3 - V_2)$$

$$W_{34} = \int_3^4 p\,dV = \frac{c}{1-\gamma}\left(V^{-\gamma+1}\right|_3^4 = \frac{1}{1-\gamma}\left(P_4V_4 - P_3V_3\right)$$

$$= \cancel{\frac{1}{1-\gamma}}$$

$W_{41} = 0$; $W_{12} = \int_1^2 p\,dV = \frac{1}{1-\gamma}\left(P_2V_2 - P_1V_1\right)$

$$\therefore\ W_{total} = P_{\underline{\underline{3}}}V_3 - P_{\underline{\underline{2}}}V_2$$

$$+ \frac{1}{1-\gamma}\left(P_4V_4 - P_{\underline{\underline{3}}}V_3\right)$$

$$+ \frac{1}{1-\gamma}\left(P_{\underline{\underline{2}}}V_2 - P_1\underline{V_1}\right)$$

$$= -\frac{1}{1-\gamma}P_1V_1 + \left[-1 + \frac{1}{1-\gamma}\right]P_2V_2$$

$$\left[-\frac{1}{1-\gamma} + 1\right]P_3V_3$$

$$+ \frac{1}{1-\gamma}P_4V_4$$

$$\Rightarrow W_{total} = -\frac{P_1V_1}{1-\gamma} + \frac{-1+\gamma+1}{1-\gamma}P_2V_2 + \frac{-1+1-\gamma}{1-\gamma}P_3V_3$$

$$+ \frac{1}{1-\gamma}P_4V_4$$

$$= -\frac{1}{1-\gamma}P_1V_1 + \frac{\gamma}{1-\gamma}P_2V_2 - \frac{\gamma}{1-\gamma}P_3V_3 + \frac{1}{1-\gamma}P_4V_4$$

The heat that enters enters during the 2→3 portion:

For this process $\Delta U = Q - W$. → $Q = \Delta U + W$.

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Now: $\overset{U}{\cancel{\Delta U}} = N \cdot f \cdot \frac{1}{2} kT$

$$\Delta U = N \cdot f \cdot \frac{1}{2} k \Delta T = \cancel{N} \cdot f \cdot \frac{1}{2} \cancel{k} \left(\frac{P_f V_f}{\cancel{N}k} - \frac{P_i V_i}{\cancel{N}k} \right)$$

$$= \frac{f}{2} (P_f V_f - P_i V_i)$$

Now $\gamma = \frac{f+2}{f}$

$f \gamma = f + 2$

$(\gamma - 1) f = 2$

$f = \frac{2}{\gamma - 1}$

$$= \frac{1}{\gamma - 1} (P_f V_f - P_i V_i)$$

Now $Q_{23} = \Delta U_{23} + W_{23}$

$$= \frac{1}{\gamma-1} (P_3 V_3 - P_2 V_2) + P_3 V_3 - P_2 V_2$$

$$= \left(\frac{1}{\gamma-1} + 1 \right) P_3 V_3 + \left(\frac{-1}{\gamma-1} - 1 \right) P_2 V_2$$

$$= \frac{1 + \gamma - 1}{\gamma - 1} P_3 V_3 - \left(\frac{1}{\gamma-1} + 1 \right) P_2 V_2$$

$$= \frac{\gamma}{\gamma-1} P_3 V_3 - \frac{\gamma}{\gamma-1} P_2 V_2$$

$$\therefore \quad e = \frac{W}{Q} = \frac{-\frac{1}{1-\gamma} P_1 V_1 + \frac{\gamma}{1-\gamma} P_2 V_2 - \frac{\gamma}{1-\gamma} P_3 V_3 + \frac{1}{1-\gamma} P_4 V_4}{-\frac{\gamma}{\gamma-1} P_2 V_2 + \frac{\gamma}{\gamma-1} P_3 V_3}$$

$$= \frac{\frac{1}{\gamma-1} P_1 V_1 - \frac{\gamma}{\gamma-1} P_2 V_2 + \frac{\gamma}{\gamma-1} P_3 V_3 - \frac{1}{\gamma-1} P_4 V_4}{-\frac{\gamma}{\gamma-1} P_2 V_2 + \frac{\gamma}{\gamma-1} P_3 V_3}$$

$$e = 1 + \frac{\frac{1}{r-1} P_1V_1 - \frac{1}{r-1} P_4V_4}{\frac{-r}{r-1} P_2V_2 + \frac{r}{r-1} P_3V_3}$$

$$= 1 + \frac{P_1V_1 - P_4V_4}{-r P_2V_2 + r P_3V_3}$$

$$= 1 - \frac{1}{r}\left[\frac{P_1V_1 - P_4V_4}{P_2V_2 - P_3V_3}\right]$$

$V_1/V_2 \, ; \, V_3/V_2 .$

$$= 1 - \frac{1}{r}\left[\frac{P_1V_1 - P_3\frac{V_3^r}{V_1^r}\cdot V_1}{P_1\frac{V_1^r}{V_2^r}\cdot V_2 - P_3V_3}\right]$$

$$P_4 \cancel{V_4} = \frac{P_3V_3^r}{V_4^r} = P_3\frac{V_3^r}{V_1^r}$$

$$P_1V_1^r = P_2V_2^r = P_3V_2^r$$

$$= 1 - \frac{1}{r}\frac{V_1}{V_2}\left[\frac{P_1 - P_3\left(\frac{V_3}{V_1}\right)^r}{P_1\left(\frac{V_1}{V_2}\right)^r - P_3\left(\frac{V_3}{V_2}\right)}\right]$$

$$\rightarrow P_3 = P_1\left(\frac{V_1}{V_2}\right)^r$$

$$P_2 = P_1\frac{V_1^r}{V_2^r}$$

$$= 1 - \frac{1}{r}\frac{V_1}{V_2}\cdot\frac{1}{\left(\frac{V_1}{V_2}\right)^r}\left[\frac{P_1 - P_3\left(\frac{V_3}{V_2}\cdot\frac{V_2}{V_1}\right)^r}{P_1 - P_3\,\frac{V_3}{V_2}\cdot\left(\frac{V_2}{V_1}\right)^r}\right]$$

$$= 1 - \frac{1}{r}\left(\frac{V_1}{V_2}\right)\left(\frac{V_2}{V_1}\right)^r\left[\frac{P_1/P_3 - \left(\frac{V_3}{V_2}\right)^r\left(\frac{V_2}{V_1}\right)^r}{P_1/P_3 - \left(\frac{V_3}{V_2}\right)\left(\frac{V_2}{V_1}\right)^r}\right]$$

7-16-02 γ

Can I express $\frac{P_1}{P_3} = F\left(\frac{V_1}{V_2}, \frac{V_3}{V_2}\right)$.

$$P_1 = P_2\left(\frac{V_2}{V_1}\right)^r = P_3\left(\frac{V_2}{V_1}\right)^r$$

$\therefore$

$$e = 1 - \frac{1}{r}\left(\frac{V_2}{V_1}\right)^{r-1} \cdot \left[\frac{\left(\frac{V_2}{V_1}\right)^r - \left(\frac{V_3}{V_2}\right)^r\left(\frac{V_2}{V_1}\right)^r}{\left(\frac{V_2}{V_1}\right)^r - \left(\frac{V_3}{V_2}\right)\left(\frac{V_2}{V_1}\right)^r}\right]$$

$$e = 1 - \frac{1}{r}\left(\frac{V_2}{V_1}\right)^{r-1} \cdot \cancel{\left(\frac{V_2}{V_1}\right)^r}\left[\frac{1 - \left(\frac{V_3}{V_2}\right)^r}{1 - \left(\frac{V_3}{V_2}\right)}\right]$$

= [illegible]

$$e = 1 - \frac{1}{r}\left(\frac{V_2}{V_1}\right)^{r-1}\left[\frac{1 - \left(\frac{V_3}{V_2}\right)^r}{1 - \left(\frac{V_3}{V_2}\right)}\right].$$

V.S. $\frac{V_3}{V_2} > 1$ $\left(\frac{V_3}{V_2}\right)^r > \left(\frac{V_3}{V_2}\right)$ $\frac{1 - \left(\frac{V_3}{V_2}\right)^r}{1 - \left(\frac{V_3}{V_2}\right)} < 1$

[illegible]

$\therefore \frac{\left(\frac{1-()^r}{1-()}\right)}{r} < 1$ $\therefore e_{desil} > e_{otto}$?

take $\frac{V_2}{V_1} = 18^{-1}$ $e_{\text{otto}} = .719$

w/ air as working substance.

$e_{\text{dil}} = .631.$

$\frac{V_3}{V_2} = 2$ $\frac{V_1}{V_2} = 18$

pg 133 Sch. [illegible]

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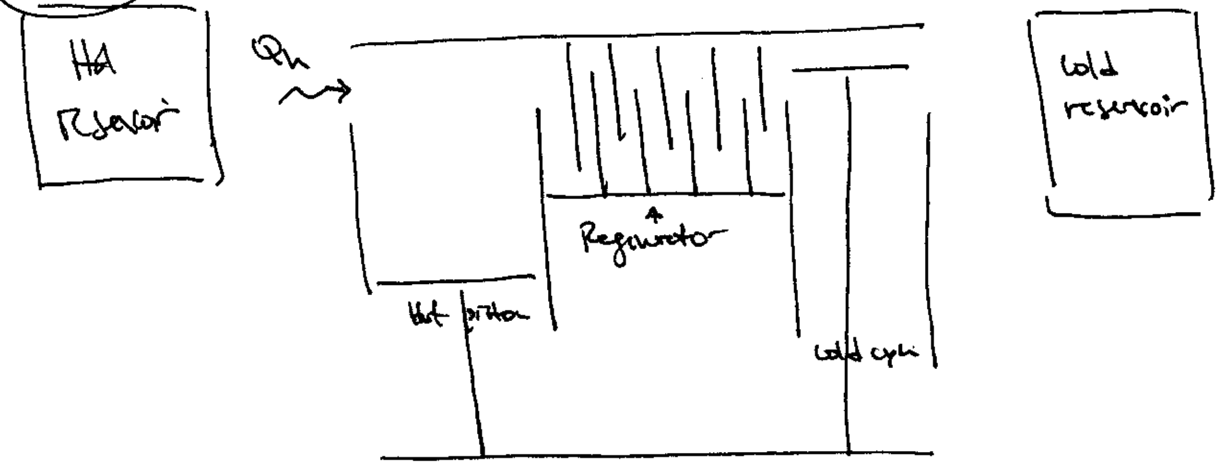
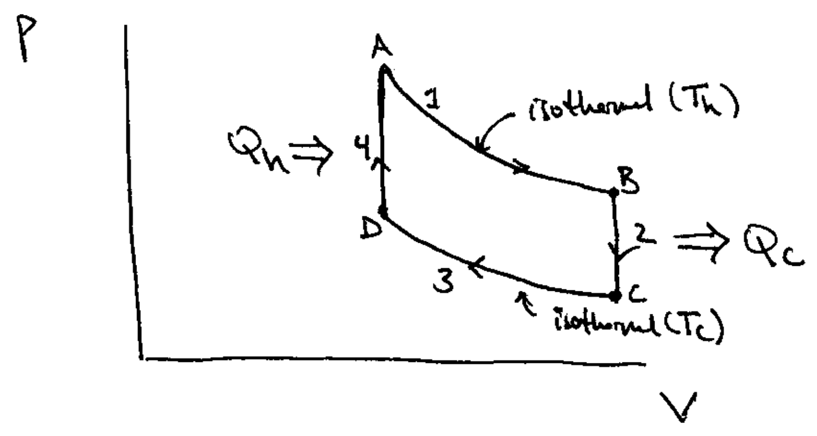
Prob 4.21



"power stroke"

(a)



$PV = \text{const}$

$P = \frac{c}{V}$.

(b) $e = \frac{W}{Q_h}$

$Q_h = \Delta U - \cancel{W}^{\,0}$.

$= \frac{f}{2} N \cdot k \Delta T$.

$$W_{AB} = \int_{AB} \cancel{PV}\, p\, dV = NkT_h \int_{AB} \frac{dV}{V} = NkT_{hot} \ln\left(\frac{V_B}{V_A}\right)$$

$$W_{CD} = NkT_{cold} \ln\left(\frac{V_D}{V_C}\right)$$

$$W_{tot} = \sum W_{\square}$$

$$e = \frac{\cancel{Nk}\left[-T_h \ln\left(\frac{V_L}{V_R}\right) + T_c \ln\left(\frac{V_L}{V_R}\right)\right]}{\left(\frac{f}{2}\right)\cancel{Nk}\left(T_h - T_c\right)}$$

$$e = \left(\frac{2}{f}\right)\frac{\left[T_h \ln\left(\frac{V_R}{V_L}\right) - T_c \ln\left(\frac{V_R}{V_L}\right)\right]}{\left(T_h - T_c\right)}$$

$$\gamma = \frac{f+2}{f}$$

$$\gamma f = f+2$$

$$(\gamma-1)f = 2$$

$$f = \frac{2}{\gamma-1}$$

$$\frac{f}{2} = \frac{1}{\gamma-1}$$

$$e = (\gamma-1)\left[\quad \ldots \quad\right]$$

$$e = (\gamma-1)\left[\frac{T_h}{T_h-T_c}\ln\left(\frac{V_R}{V_L}\right) - \frac{T_c}{T_h-T_c}\ln\left(\frac{V_R}{V_L}\right)\right]$$

$\Rightarrow$ $e = (\gamma-1)\ln\left(\frac{V_R}{V_L}\right)$ This doesn't seem correct...

(c) What is the regenerators purpose? To simply hold heat?

(d) ?

$$\Delta U = Q - PdV.$$

$$dU = đQ - PdV$$

$$dU + PdV = đQ$$

$$\rightarrow d(U + PV)\Big|_P = đQ.$$

$$dH\Big|_P = đQ. \quad \rightarrow \quad \Delta H\Big|_P = đQ$$

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} \qquad Q_h = W + Q_c$$

$$= 1 - \frac{Q_c}{Q_h}$$

$$= \cancel{1 - \frac{H_1 - H_4}{H_3 - H_2}} = \cancel{1 - \frac{H_4 - H_1}{H_2 - H_2}}$$

$$= \cancel{g \; H_2}$$

Now $Q_h = \Delta H_{23} = H_3 - H_2$

$Q_c = \Delta H_{41} = H_4 - H_1$

$$\therefore \quad e = 1 - \frac{H_4 - H_1}{H_3 - H_2} \approx 1 - \frac{H_4 - H_1}{H_3 - H_1}$$

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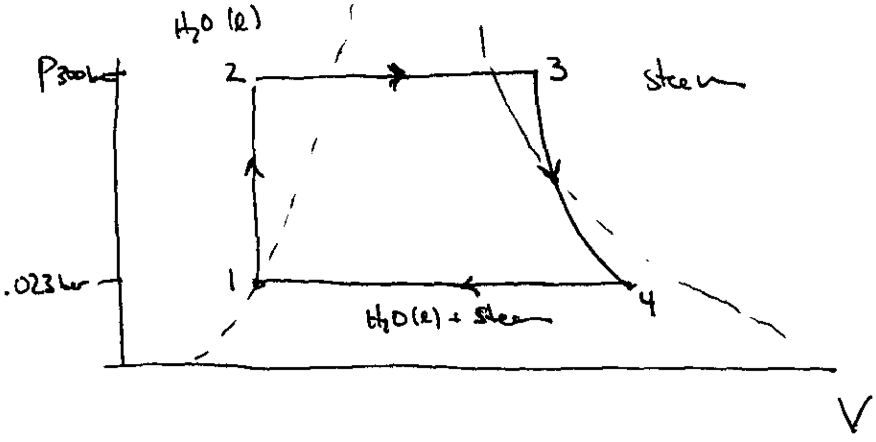
$H_4 = ?$

look up entropy at pt ~~B3~~ 3 + then using that entropy, look up H from table 4.1 (sat. H_2O steam)



$H_1 = 84$ kJ $H_3 = 3444$ kJ

entropy at 3 = 6.233 kJ/K → pt 4 in H_2O(l) + steam at

$$\overset{H_2O}{x(.297)} + \overset{\text{steam}}{(1-x)(8.667)} = 6.233$$

$$(.297 - 8.667)x = 6.233 - 8.667 =$$

$x = .2908$ of H_2O

+ $1-x = .71$ of steam

This mix has

H_4(kJ) $= .29(84) + (.71)(2538) = 1826.3$

$$e = 1 - \frac{(1826.3 - 84)}{(3444 - 84)} = .481 \ldots$$

$$e_{carnot} = \cancel{1 - \frac{T_h}{T_c}} \; 1 - \frac{T_c}{T_h} = 1 - \frac{20+273}{600+273} = \cancel{.998} \; .66.$$

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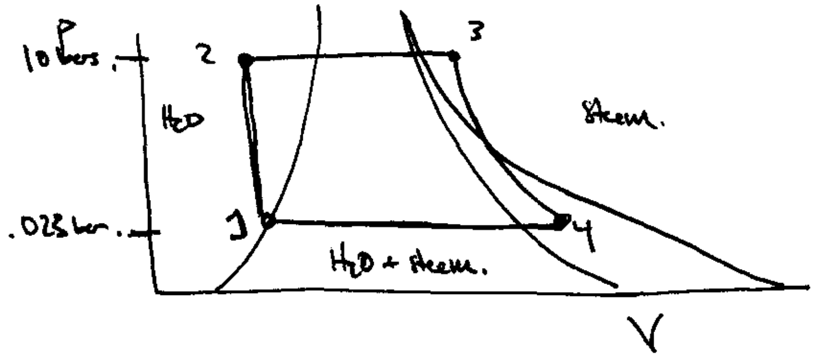
Prob 4.22

$$e \hat{=} 1 - \frac{H_4 - H_1}{H_3 - H_1}$$



$H_1 = 84$ kJ. $H_3 = 3051$ kJ

$H_4 = ?$

$S_3 = S_4 = 7.123 = .297 x_{H_2O} + 8.667(1 - x_{H_2O})$

$\Rightarrow$ ~~x_{H_2O}~~ [illegible]

$x_{H_2O} = . .$

~~8.667~~ +

$-8.37 x_{H_2O} = -1.544$

$x_{H_2O} = .184 \leftarrow$

$1 - x_{H_2O} = .81 \leftarrow$

Then $H_4 = (.184)84 + (.81)(2538) = . .$

Prob 4.23 $H \equiv U + PV$. $\Delta H = \Delta U + P\Delta V$

$H_2 = H_4 + \Delta H$

?

$dH = đQ$

$\frac{dH}{T} = \frac{đQ}{T} = dS$

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Prob 4.24

(a) $e \cong 1 - \frac{H_4 - H_1}{H_3 - H_1}$ $P_{max} = 300$ bars

$T_{max} = 800$ then $H_2 + H_3$ change

$H_3 = 3081$ kJ

$$e \cong 1 - \frac{1824 - 84}{3081 - 84} = .419$$

(b) $P_{max} = 100$ bars. then $H_2 + H_3$ change

$H_3 = 3628$

$$e \cong 1 - \frac{1824 - 84}{3625 - 84} = .508$$

(c) $T_{min} = 10^\circ C$ ⇒ $H_1 + H_4$ change.
(H₂O) p_{min} = ~~.023~~ .01 bar

$H_1 = 42$ kJ.

w/ $S_3 = 6.233$ kJ/K
$\uparrow$
still

$$x_{H_2O}(.151) + (1 - x_{H_2O})(8.901) = 6.233$$
$\Rightarrow x_{H_2O} = .304$ $1 - x_{H_2O} \cong .7$

$$H_4 = .3(42) + .7(2520)$$

$$= 1776 \text{ kJ}.$$

$$e \cong 1 - \frac{1776 - 84}{3444 - 84} = .496$$

(P 4.25) in going from pt 3 full steam to H_2O + steam an ~~the~~ increase in entropy is to be expected. Since steam has so much more entropy then H_2O, this increase in entropy prob. shows itself as an increase in the amount of steam present. Thus x_{H_2O} (mass fraction of liquid H_2O) is less then expected

⇒ more steam ⇒ causes the ~~enthalpy~~ enthalpy of H_4 to increase <u>Lowering</u> the ~~[illegible]~~ efficiency of the steam engine.

$$\left\{ B = -V \frac{\partial P}{\partial V} \right\}$$

(P 4.26) $W = 10^9$ W.

$$.4 \cong e = \frac{\dot{W}}{\dot{Q}_h}$$

$$\dot{Q}_h = H_3 \times H_2 \approx H_3 \times H_1$$

$$= (l_{kg})\dot{M}$$

$$@\ l = 2260 \text{ J/g}$$

$$= 2260 \cdot \frac{10^3 \text{ J}}{\text{kg}}$$

$$\underline{\dot{M}} = \frac{(\dot{W}/e)}{\ell} \qquad [illegible] =$$

(P 4.27) ? T + P don't increase at the same rate.
P is increasing faster than T + ∴ applying more pressure "squeezes" the entropy.

(P.4.28) ?

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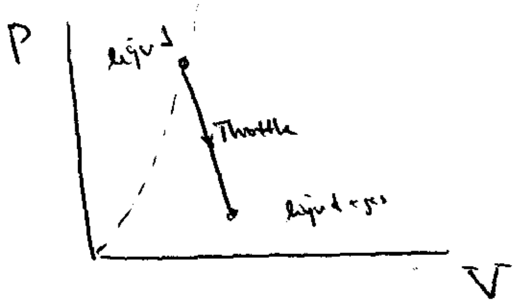
Prob 4.29 When throttled $H_1 = H_2$



$H_{liquid}(12 \text{ bars}) = 116 \text{ kJ}$

$= H(1 \text{ bar}) = x H_{liquid} + (1-x) H_{gas}$

$= x(16) + (1-x)(231)$

$\Rightarrow x = .53 \qquad 1-x = .4651$

fraction of liquid fraction vaporized

$T_{final} = -26.4 °C$

Prob 4.30

(a) ~~S(10 bars)~~.

Assuming all initially is gas $S(1 \text{ bar}) = .94 \text{ kJ/K}$

then compressing adiabatically to 10 bars requires the final temperature of the superheated (gaseous) reactant

$S = S(T)$

$$S = .907 + \frac{(.943 - .907)}{(50-40)}(T-40) \Rightarrow S = .94 \text{ gives } T = 322.16 \text{ K}$$

$= 49.16 °C$

(b) At pt 2 $H_2 =$ ~~[illegible]~~

$$274 + \frac{(284-274)}{(50-40)}(49.16-40)$$

$$= 283.16 \text{ kJ} \qquad T = 49.16°C$$

At pt 1 $H_1 = 231$ kJ $\qquad T = -26.4°C$

Assuming we have
all vapor

At pt 3 $H_3 = 105$ kJ $\qquad T = 39.4$

Assuming we have
all liquid

At pt 4: Throttling requires $\underline{H_3} = \underline{H_4}$ $\qquad T = -26.4$

$H_3 = 105 = x(16) + (1-x)\cdot 231$

$$\therefore \underset{\text{liquid}}{x = .586} \qquad \underset{\text{vapor}}{1-x = .4139}$$

$$\therefore \text{COP} = \frac{H_1 - H_3}{H_2 - H_1} = \frac{231 - 105}{283.16 - 231} = 2.415 > 1 \ ?$$

$$e_{carnot} = 1 - \frac{T_c}{T_h} = 1 - \left(\frac{273 - 26.4}{273 + 49.16}\right) =$$

Both temperatures seem a bit to large/small

(c) .4139

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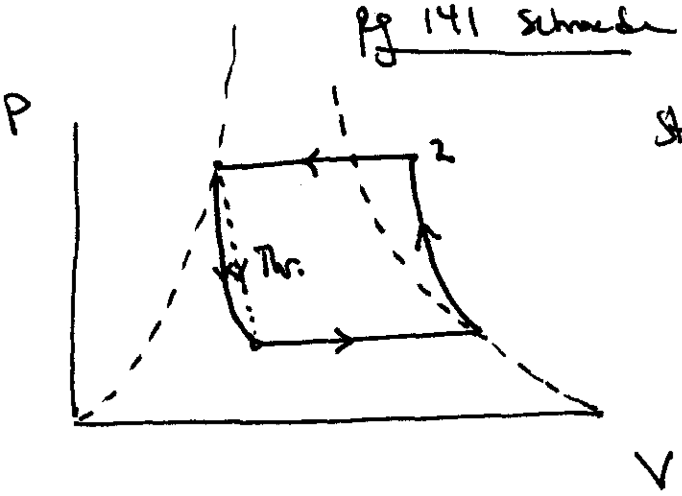
P. 4.31



Standard refrigeration cycle ...

?

P.4.32 I would prob. have it operate between 1bar - 12 bars pressure difference ... As the other problems did.

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Prob 4.33

(a) $T_i = 300k$

$P_i = 100 bars$

$H_i =$ [illegible] 8174 J

$$= \frac{(5800-8717)}{(200-300)}(T-300) + 8717 = 8174$$

$\Rightarrow T = 281.3 k.$

(b) $H_i = 4442 J.$

~~$= \frac{(4442+1946)}{(200-100)}(T-100) + 1946$~~

[illegible]

$$= \frac{(5800-2856)}{(200-100)}(T-100) + 2856$$

$\Rightarrow$ [illegible] $4442 = 29.44(T-100) + 2856$

$T = 153.87 k$

(c) $H_i = -1946$ $T_{final} = 77 k$

$= x(-3407) + (1-x)(2161)$

$\Rightarrow$ ~~$.339 \Rightarrow x$~~ $-1946 = -5.56 \cdot 10^3 x + 2161 \Rightarrow x = .737$ liquid

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(d) ~~[illegible]~~

$$H_{f_{\text{limit}}} = (.00\cdots01)(-3407) + (.99\cdots9)(2161)$$

$$\rightarrow 2161 \text{ J}$$

$$\Rightarrow \quad 2161 \text{ J} = \frac{4442+1946}{(200-100)}(T-100) + -1946$$

$$= 63.8(T-100) - 1946$$

$$T = \underline{164}.37 \text{ K}$$

(e) The temperature after throttling would increase. because we have to get an increased entropy

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Prob 4.34

(a) Constant enthalpy process happen whenever ~~one~~ ~~this~~ transformations take place at constant pressure ... ~~I~~ ~~believe~~ ~~this~~ ~~process~~ & no heat flows into or out of the system. Since the heat flow by the heat exchanger is self contained. I claim that this is a constant enthalpy process

$$H = U + pV$$

$$dH = dU + p\,dV$$

$$H_{in} = x H_{liquid} + (1-x) H_{gas}$$

$$= x(H_{liquid} - H_{gas}) + H_{gas}$$

$$X = \frac{H_{in} - H_{gas}}{H_{liquid} - H_{gas}}$$ ~~so.~~ ~~How~~ ~~get~~

$$= \frac{H_{in} - H_{out}}{H_{liq} - H_{out}} = \frac{H_{out} - H_{in}}{H_{out} - H_{liq}}$$ since $H_{out} = H_{gas}$

(c) 1 bar — 100 bars

$T_{in} = 300k$ $T_{out} = 300k$

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$$X = \frac{8717 - 8174}{8717 - (-3407)} = .0447 \sim 4\%$$

if T = 200 K

$$X = \frac{8800 - 4442}{8800 - (-3407)} = .147 \sim 15\%$$

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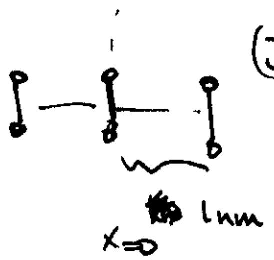
P. 4.35



$\left(\frac{\mu_0}{4\pi}\right)\frac{\mu}{r^3}$ $\mu_0 = 4\pi \cdot 10^{-7}$

$\mu = 1.9 \cdot 10^{-24}\, J/T$

(a) $$2\sum_{P.E.\,r_i}\left(\frac{\mu_0}{4\pi}\right)\frac{\mu}{r_i^3} = 2\frac{\mu_0}{4\pi}\mu\sum_{i=1}^{\infty}\frac{1}{(10^{-9})^3 i^3}$$ $i^{-3} \rightarrow \frac{i^{-2}}{-2}$

$$\cong 2\frac{\mu_0\mu}{4\pi}\cdot(10^9)^3\left(\frac{-1}{2i^2}\right|_1^\infty$$

$$\cong \cancel{2}\frac{\mu_0\mu}{4\pi}\frac{(10^9)^3}{\cancel{2}}$$

$$= 10^{-7}\cdot(10^{-24}\cdot 9)(10^{27}) \overset{?}{=} 9\cdot 10^{-4}\ J/T$$ units?

(b) $B = 1T$

From argument given on pg 145

$\frac{M}{\mu N} = .57$ w/ M $\underline{\underline{\text{fixed}}}$ & lowering B to that point

due to molecules themselves or about 10,000

so from $T_i = 300K$ to $T_f = \frac{3}{100} = .03\ K$

(c) ?

(d) Again this argument about difficulty of getting very low temp + very stable systems?

Prob 4.36

$$p = \frac{h}{\lambda} = \hbar k \qquad U = N \cdot f\left(\tfrac{1}{2}k_B T\right)$$

recoil energy is loss of momentum derived from laser

$$KE = \frac{1}{2}\frac{p^2}{m}$$

$$\frac{f}{2}k_B T = \frac{1}{2}\frac{1}{m}\left(\frac{h^2}{\lambda^2}\right) \qquad \text{for solids } f = 6.$$

$$T = \frac{1}{f}\frac{1}{m k_B}\left(\frac{h^2}{\lambda^2}\right)$$

$$= \frac{1}{6}\frac{1}{(1.419\cdot 10^{-22}\cdot 10^{-3}\ \text{kg/atom})}\cdot$$

$$\frac{85.46\ \text{g/mol}}{6.022\cdot 10^{23}\ \text{atoms/mol}}$$

$$= 1.419\cdot 10^{-22}\ \text{g/atom}$$

$\cdot 1.$

$$T = \frac{1}{6(1.419\cdot 10^{-22}\cdot 10^{-3}\ \text{kg/atom})(1.381\cdot 10^{-23}\ \text{J/K})}\frac{(6.626\cdot 10^{-34}\ \text{J}\cdot\text{s})^2}{(780\cdot 10^{-9})^2}$$

$$= 6.136\cdot 10^{-11}\ \text{K}.$$

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Prob 4.37 One certainly cannot go as low as $T=0$.

Don't fully understand question asked. ..

Pg 152 Schroeder 9-30-02

$$V_{(1)} = \frac{(1)(8.314\ \text{J}/\text{mol}\cdot\text{K})(300\ \text{K})}{10^{5}\ \text{Pa}}$$

$$\cong \frac{2400\ \text{J}}{10^{5}\ \text{Pa}}$$

$$\Delta V = \frac{2400}{10^{5}}\left(\frac{\text{J}}{\text{Pa}}\right)$$

So $P\Delta V \cong 2.4\ \text{kJ}$ How get 4 kJ?

Pg 152 Schroeder 9-30-02

Prob 5.1

$P = 1\text{atm} = 10^5$ Pa

$T = 300K$

$V = \frac{(1)RT}{P}$ ✓

$U_{\text{thermal}} = 7 \cdot N \cdot \frac{1}{2}kT = $ ✓.

$S = \cancel{Fk\ln}\ Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$

$H = U + PV$

$F = U - TS$

$G = U + PV - TS$.

Prob 5.2

$N_2 + 3H_2 \rightarrow 2NH_3$

$\Delta H = ?$

$\cancel{\Delta H(N_2 \rightarrow 2N) = 0}$

$\cancel{\Delta H(H_2 \rightarrow 2H) = 0}$

$\Delta H(NH_3 \rightarrow N + 3H) = \Delta H(NH_3 \rightarrow \cancel{\tfrac{1}{2}N_2 +} \tfrac{3}{2}H_2)$

$=$

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$\Delta H(NH_3) = -46.11$ kJ

$S(NH_3) = 192.45$ J/K

[illegible] =

[illegible] =

ΔG(Formation of NH_3 from $N_2 + H_2$) = [illegible] 2(−46.11 kJ) + $T\Delta S$

= −92.22 kJ + 298 (192.45 J)·2

= [illegible] 2248 kJ. ≠ −16. kJ.

Whats wrong?

(P 5.3) $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \to 2PbSO_4 + 2H_2O$

$\Delta H = -316$ kJ/mol

$\Delta H =$ ~~ΔH~~ $2(-920) + 2(-285.83)$

$- 0 - (-277.4) - 0 - 2(-909.3)$

$= -315.6$ kJ/mol ✓.

$\Delta G = 2(-813) + 2(-237.13) - 0 - (-217.33) - 4(0) - 2(-744.53)$

$= -393.8$ kJ.

(P. 5.4) Electrolosis of H_2O requires

$\Delta G = 237$ kJ of electrical work input by U.S.

(Additional "work" can come from heat flow inward)

$$\frac{237 \text{ kJ/mol}}{2 \cdot 6.02 \cdot 10^{23} \text{/mol}} = 1.96 \cdot 10^{-19} \text{ J}$$

$\{1 \text{ J} = 6.2 \cdot 10^{18} \text{ eV}\}$ $= 1.22$ eV.

= ~~[illegible]~~. 1.22 Volts. would think that this would be the minimum

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pg 155 Schroeder

Prob 5.5

(a) $CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2$

$\Delta H = -393.51 + 2(-\underbrace{241.82}) - (-74.81) - 2(0)$ (kJ)

$= \cdots$

↑ the assumption that this is a gas maybe incorrect if the reaction takes place at standard temp + pressure. because in that range the H_2O would be a liquid...

$\Delta G = (-394.36) + 2(-228.57) - (-50.72) - 2(0)$ (kJ)

$= \cdots$

(a) So

$\Delta H = -802.34$ kJ

+ $\Delta G = -800.78$ kJ

(b) From eq 5.8 $\Delta G \leq W_{other}$

$\therefore$ electrical energy available $\overset{?}{\leq} -800.78$ kJ

(c) $\Delta G = \Delta H - T\Delta S$ w/ $T\Delta S$ entering as heat

$\therefore T\Delta S = \Delta H - \Delta G = -802.34 - (-800.78) = 1.56$ kJ.

(d) Thus 8 electrons go around ∀ ~~[illegible]~~ reaction step

Thus obtaining $\dfrac{800.78 \text{ kJ}}{8 \cdot 6.02 \cdot 10^{23}} = 1.66 \cdot 10^{-19} \text{ J} = 1.037 \text{ eV}$

$\Rightarrow$ 1 Volt cell

$1 \text{J} = 6.2421 \cdot 10^{18} \text{ eV}$

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Pg 156 Schroeder

Prob 5.6

(a) $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

$$\Delta H = 6(-393.51) + 6(-285.83) - (-1273) - 6.0$$
$$= -2803 \text{ kJ}$$

$$\Delta G = 6(-394.36) + 6(-237.13) - (-910) - 6.0$$
$$= -2878.94 \text{ kJ.}$$

(b) Max work a muscle can perform is 2878.94 kJ work (electrical)

(c) $\Delta G = \Delta H - T\Delta S$

$\Rightarrow T\Delta S = \Delta H - \Delta G = -2803 + 2878.94 = 75.94$ kJ.

comes from heat <u>absorbed</u> into the cell.

(d) ?

(e) The work the muscle could do would be less than 2878.94 kJ

+ the heat absorbed ... less also?

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Pg 156 Schroeder

Prob 5.7

$$\langle F \rangle = 4\cdot 10^{-12}\ \text{N}.$$

$$d \cong 11\cdot 10^{-9}\ \text{m}$$

$$W = (4\cdot 10^{-12}\cdot 11\cdot 10^{-9})\,\text{J} = (4.4\cdot 10^{-20})\,\text{J}$$

$$e = \frac{W}{W_{max}} = \frac{(4.4\cdot 10^{-20})\,\text{J}}{\frac{(2878.94\cdot 10^{3}\,\text{J})}{6.02\cdot 10^{23}}} = 9.2\cdot 10^{-3}$$

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(Prob 5.8)

$$G = U + PV - TS$$

$$dG = dU + dP\cdot V + PdV - dT\cdot S - TdS$$

$$= T\cancel{dS} - P\cancel{dV} + \mu dN + V\cdot dP + P\cancel{dV} - SdT - T\cancel{dS}$$

$$= VdP - SdT + \mu dN$$

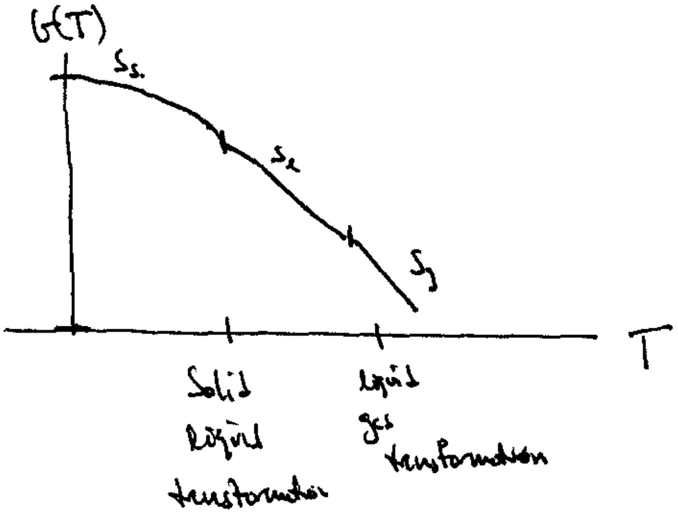
$$= -SdT + VdP + \mu dN \qquad \text{eq } 5.23$$

$$\left.\frac{\partial G}{\partial T}\right|_{P,N} = -S \;;\; \left.\frac{\partial G}{\partial P}\right|_{T,N} = V \;;\; \left.\frac{\partial G}{\partial N}\right|_{T,P} = \mu$$

$$S = -\left.\frac{\partial G}{\partial T}\right|_{P,N} \;;\; V = \left.\frac{\partial G}{\partial P}\right|_{T,N} \;)\; \mu = \left.\frac{\partial G}{\partial N}\right|_{T,P}$$

(Prob 5.9)

$$dG = -S\,dT + V\,dP + \mu\,dN \qquad S \geq 0$$



$P = \text{const}$ + $N = \text{const}$

$$\Rightarrow \quad dG = -S\,dT$$

$$S_{solid} \leq S_{liquid} \leq S_{gas}$$

Prob 5.10

$\Delta T = 5°C = 5K$

$\Delta G \cong -S\Delta T + V\overset{0}{\cancel{\Delta P}} + \mu\overset{0}{\cancel{\Delta N}}$

$S_{H_2O\ S.T.P.} = 69.91\ J/K$

$\therefore\ \Delta G \cong (-69.91)(5) = -349.55\ J$

$\Delta G = 0 = -349.55 + V\Delta P$

$V\Delta P = 349.55\ J$

$\parallel$

$(18.068\ cm^3)(\Delta P) =$

$1cm = 10^{-2} m$

$(18.068(10^{-2})^3 m^3)\ \Delta P = 349.55\ J$

$\Delta P = 1.934 \cdot 10^7\ J/m^3$

$J = N \cdot m$

$= 1.934 \cdot 10^7\ Pa.$

$1atm = 1.013 \cdot 10^5\ Pa$

$= 190.9\ atm.$

$\Rightarrow 1Pa = 9.87 \cdot 10^{-6}\ atm$

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Prob 5.11

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$

$\Delta H = 286$ kJ

$\Delta G = 237$ kJ

$dG = -S\,dT + V\,dP + \mu\,dN$

$S_{H_2O} = 70\ J/K$ $S_{H_2} = 131\ J/K$ $S_{O_2} = 205\ J/K$ $\Big\}$ at ~~atm~~ P = 1atm, T = 25°C

$G_{H_2O} = 237$ kJ $G_{H_2} = 0$ $G_{O_2} = 0$

(a) $\Delta G_{H_2} \cong -S\Delta T = (-131)(50) = -6.55$ kJ

$\Delta G_{H_2O} \cong -S\Delta T = -(70)(50) = -3,5$ kJ

$\Delta G_{O_2} \cong -(205)(50) = -10,25$ kJ

$\therefore$ $G_{H_2} = -6,55$ kJ $G_{O_2} = -10,25$ kJ $G_{H_2O} =$ ~~3.~~ $237 - 3,5$

$= 233,5$ kJ

(b) Then $\Delta G_{cycle} = G_{H_2} + \frac{1}{2}G_{O_2} - G_{H_2O}$

$= -6,55 + \frac{1}{2}(-10,25) - (233,5$

..., is there a sign error?

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Prob 5.12

$$dU = TdS - pdV + \mu dN$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial p}{\partial S}\right|_V$$

$$dH = TdS + Vdp + \mu dN$$

Note: $\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)$

$$\Rightarrow \quad \left.\frac{\partial T}{\partial p}\right|_S = \left.\frac{\partial V}{\partial S}\right|_p$$

$$dF = -SdT - PdV + \mu dN$$

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)$$

$$\|$$

$$-\left.\frac{\partial S}{\partial V}\right|_T = -\left.\frac{\partial p}{\partial T}\right|_V \quad \Rightarrow \quad \left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V$$

$$dG = -SdT + Vdp + \mu dN$$

$$\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)$$

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$$\frac{\partial}{\partial p}(-S)\Big|_T = \frac{\partial}{\partial T}(V)\Big|_p$$

$$\Rightarrow -\frac{\partial S}{\partial p}\Big|_T = \frac{\partial V}{\partial T}\Big|_p$$

Prob 5.13 $\beta \equiv \frac{1}{V}\frac{\partial V}{\partial T}\Big|_{p}$?

relate V ~ S Then by the 4th identity

$\beta = \frac{1}{V}\left(-\frac{\partial S}{\partial p}\right)\Big|_T$ How do I know $\frac{\partial S}{\partial p} = 0$ when $T=0$?

Prob 5.14 Prob 3.33 $\Rightarrow$ $C_V = T\frac{\partial S}{\partial T}\Big|_V$

$$dS = \frac{\partial S}{\partial T}\Big|_V dT + \frac{\partial S}{\partial V}\Big|_T dV = \frac{C_V}{T}dT + \frac{\partial S}{\partial V}\Big|_T dV$$

$$dV = \frac{\partial V}{\partial T}\Big|_p dT + \frac{\partial V}{\partial p}\Big|_T dp$$

$$dS = \cancel{\frac{C_V}{T}}\cancel{dT} \;\; \frac{C_V}{T}dT + \frac{\partial S}{\partial V}\Big|_T\left(\frac{\partial V}{\partial T}\Big|_p dT + \frac{\partial V}{\partial p}\Big|_T dp\right)$$

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$$dS = \left(\frac{C_V}{T} + \frac{\partial S}{\partial V}\Big|_T \frac{\partial V}{\partial T}\Big|_p \right) dT + \left(\frac{\partial S}{\partial V}\Big|_T \frac{\partial V}{\partial P}\Big|_T \right) dP$$

if $dP = 0$

$$\frac{\partial S}{\partial T}\Big|_p = \frac{C_V}{T} + \frac{\partial S}{\partial V}\Big|_T \frac{\partial V}{\partial T}\Big|_p \qquad \frac{\partial S}{\partial T}\Big|_p =$$

$$Q_p = \cancel{\frac{\Delta S}{T}}\Big|_p \qquad \Delta S|_p = \frac{Q|_p}{T} \Rightarrow Q_p = T \Delta S$$

$$C_p = \frac{Q_p}{\Delta T} = \frac{1}{T} \frac{\partial S}{\partial T}\Big|_p \qquad C_p = \frac{Q_p}{\Delta T} = T \frac{\partial S}{\partial T}\Big|_p$$

$$\Rightarrow \frac{\partial S}{\partial T}\Big|_p = \frac{1}{T} C_p.$$

$\therefore$

$$\frac{C_p}{T} = \frac{C_V}{T} + \frac{\partial S}{\partial V}\Big|_T \frac{\partial V}{\partial T}\Big|_p$$

$$C_p - C_V = T \frac{\partial S}{\partial V}\Big|_T \frac{\partial V}{\partial T}\Big|_p$$

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)$$

$$-\frac{\partial S}{\partial V}\Big|_T = -\frac{\partial P}{\partial T}\Big|_V$$

(c) Now [illegible] $\beta \equiv \frac{1}{V} \frac{\partial V}{\partial T}\Big|_p$ $\Rightarrow \frac{\partial S}{\partial V}\Big|_T = \frac{\partial P}{\partial T}\Big|_V$

thermal expansion coefficient

$$\cancel{B_T} \leq \kappa_T \equiv -\frac{1}{V} \frac{\partial V}{\partial P}\Big|_T$$

$\therefore$

$$C_p - C_V = T V \beta \frac{\partial S}{\partial V}\Big|_T$$

$$C_p - C_v = TV\beta \left.\frac{\partial P}{\partial T}\right|_V$$

considering P, V, + T as variables ...

$$\left.\frac{\partial P}{\partial V}\right|_T \cdot \left.\frac{\partial V}{\partial T}\right|_P \cdot \left.\frac{\partial T}{\partial P}\right|_V = -1 \quad \Rightarrow \quad \left.\frac{\partial P}{\partial T}\right|_V = -\left.\frac{\partial P}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P$$

$$= -V\left.\frac{\partial P}{\partial V}\right|_T \cdot \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$$

$$= \frac{\beta}{\kappa_T}$$

∴ ~~$C_p - C_v = TV\beta\left(-\frac{\partial P}{\partial}\right.$~~

∴

$$C_p - C_v = \frac{TV\beta^2}{\kappa_T}$$

(d) For an ideal gas $PV = NkT \Rightarrow V = \frac{NkT}{P}$

$$\beta \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P = \frac{1}{V}\left(\frac{Nk}{P}\right) = \frac{1}{T}$$

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T = -\frac{1}{V}\left(\frac{NkT}{P^2}\right)(-1) = \frac{NkT}{VP\cdot P} = \frac{1}{P}$$

$$C_p = \left.\frac{\partial H}{\partial T}\right|_V \qquad H = \left(\frac{f+2}{2}\right)NkT \qquad \left.\frac{\partial H}{\partial T}\right|_V = \left(\frac{f+2}{2}\right)Nk$$

$$C_v = \left.\frac{\partial U}{\partial T}\right|_V \qquad U = f \cdot N \cdot \tfrac{1}{2}kT$$

$$\frac{\partial U}{\partial T} = fN\tfrac{1}{2}k$$

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$$C_p - C_V = \left(\frac{f+2}{2}\right)Nk - \frac{f}{2}Nk = Nk$$

$$\overset{?}{=} \frac{T\cdot V\cdot (1/T)^2}{(1/P)} = \frac{PV}{T} = Nk \ \checkmark$$

(e) $C_p - C_V \geq 0$

$C_p \geq C_V$.

(f) H_2O (25°C)

$\beta = 2.57\cdot 10^{-4}\ K^{-1}$

$\kappa_T = 4.52\cdot 10^{-10}\ Pa^{-1}$

$V = 18.068\cdot 10^{-6}\ m^3$

Hg (25°C)

$\beta = 1.81\cdot 10^{-4}\ K^{-1}$

$\kappa_T = 4.04\cdot 10^{-11}\ Pa$

$V = 14.81\cdot 10^{-6}\ m^3$

So

$$\frac{TV\beta^2}{\kappa_T} = .744\left(\frac{K\cdot m^3\cdot K^{-2}}{Pa^{-1}}\right) \qquad \frac{TV\beta^2}{\kappa_T} = 3.578\ (J/K)$$

$$K^{-1} m^3 \left(\frac{N}{m^2}\right)$$

$$K^{-1} m N$$

$$\frac{J}{K}$$

By ≈ 300% / 380.9%

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(9) $C_p - C_V = \frac{TV\beta^2}{\kappa_T}$

$\beta = \beta(T)$

when T is small the difference between C_p + C_V is small.

but for larger T's the differen is larger

Prob 5.15 $C_p = \frac{\partial H}{\partial T}\Big|_p \qquad C_V = \frac{\partial U}{\partial T}\Big|_V$

$$C_p - C_V = \frac{\partial H}{\partial T}\Big|_p - \frac{\partial U}{\partial T}\Big|_V \qquad H = U + PV.$$

$$= \frac{\partial (U + PV)}{\partial T}\Big|_p - \frac{\partial U}{\partial T}\Big|_V$$

$$= \frac{\partial U}{\partial T}\Big|_p + \frac{\partial (PV)}{\partial T}\Big|_p - \frac{\partial U}{\partial T}\Big|_V$$

$$= \frac{\partial U}{\partial T}\Big|_p + P\frac{\partial V}{\partial T}\Big|_p - \frac{\partial U}{\partial T}\Big|_V$$

Fr $dU = S\,dT - p\,dV + \mu\,dN$

Don't see?

Prob 5.16

$$\kappa_T = \kappa_S + \frac{TV\beta^2}{C_P} \qquad \kappa_S = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_S$$

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T$$

~~Consider~~ $V = \cancel{V(T,S)}$

$\cancel{dV = \frac{\partial V}{\partial T}\Big|_S dT + \frac{\partial V}{}}$

~~Consider~~ $\cancel{V = V(P,T)}$

$\cancel{dV = \frac{\partial V}{\partial P}\Big|_T dP + \frac{\partial V}{\partial T}\Big|_P dT}$

$$C_V = T\frac{\partial S}{\partial T}\Big|_V$$

$$C_P = T\frac{\partial S}{\partial T}\Big|_P$$

consider $V = V(P,S)$

$$dV = \frac{\partial V}{\partial P}\Big|_S dP + \frac{\partial V}{\partial S}\Big|_P dS$$

Now consider S to be a function of P + T

$$dS = \frac{\partial S}{\partial P}\Big|_T dP + \frac{\partial S}{\partial T}\Big|_P dT$$

$$dV = \frac{\partial V}{\partial P}\Big|_S dP + \frac{\partial V}{\partial S}\Big|_P \frac{\partial S}{\partial P}\Big|_T dP + \cancelto{0 \ \ T\text{ const}}{\frac{\partial V}{\partial S}\Big|_P \frac{\partial S}{\partial T}\Big|_P dT}$$

$$\frac{\partial V}{\partial P}\Big|_T = \frac{\partial V}{\partial P}\Big|_S + \frac{\partial V}{\partial S}\Big|_P \frac{\partial S}{\partial P}\Big|_T$$

$$-V\kappa_T = -V\kappa_S + \left.\frac{\partial V}{\partial S}\right|_p \cdot \left.\frac{\partial S}{\partial p}\right|_T$$

Now $$\left.\frac{\partial S}{\partial p}\right|_T \cdot \left.\frac{\partial T}{\partial S}\right|_p \cdot \left.\frac{\partial p}{\partial T}\right|_S = -1$$

$$\Rightarrow \quad \left.\frac{\partial S}{\partial p}\right|_T = \frac{-1}{\left.\frac{\partial T}{\partial S}\right|_p \cdot \left.\frac{\partial p}{\partial T}\right|_S}$$

$$-V\kappa_T = -V\kappa_S - \frac{\partial V/\partial S|_p}{\left.\frac{\partial T}{\partial S}\right|_p \left.\frac{\partial p}{\partial T}\right|_S}$$

$$\beta \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p$$

$$\left.\frac{\partial V}{\partial S}\right|_p = \left.\frac{\partial V}{\partial T}\right|_p \cdot \left.\frac{\partial T}{\partial S}\right|_p = V\beta \left.\frac{\partial T}{\partial S}\right|_p$$

$$-V\kappa_T = -V\kappa_S - \frac{V\beta}{\left.\frac{\partial p}{\partial T}\right|_S}$$

$$\kappa_T = \kappa_S + \frac{\beta}{\left.\frac{\partial p}{\partial T}\right|_S}$$

$$C_p = T\left.\frac{\partial S}{\partial T}\right|_p$$

$$\boxed{\left.\frac{\partial p}{\partial T}\right|_S} \left.\frac{\partial T}{\partial S}\right|_p \cdot \left.\frac{\partial S}{\partial p}\right|_T = -1$$

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$$\kappa_T = \kappa_S + \frac{-\beta}{\left(\frac{\partial T}{\partial S}\Big|_p \cdot \frac{\partial S}{\partial P}\Big|_T\right)^{-1}}$$

$$\kappa_T = \kappa_S - \beta \left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial S}{\partial P}\Big|_T\right)$$

$$\frac{C_p}{T} = \frac{\partial S}{\partial T}\Big|_p$$

$$= \kappa_S - \frac{\beta T}{C_p} \cdot \frac{\partial S}{\partial P}\Big|_T$$

Show $\frac{\partial S}{\partial P}\Big|_T = -\beta V$ $\qquad \beta = \cancel{\frac{1}{V}\frac{\partial P}{\partial}}\ \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p$

$$= -\frac{\partial V}{\partial T}\Big|_p$$

Is this a maxwell relation?

$$dU = TdS - pdV + \mu dN$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

$$\|$$

$$\frac{\partial}{\partial V}(T)\Big|_S = \frac{\partial}{\partial S}(-p)\Big|_V \Rightarrow \frac{\partial T}{\partial V}\Big|_S = -\frac{\partial P}{\partial S}\Big|_V$$

$$\frac{\partial V}{\partial T}\Big|_S = -\frac{\partial S}{\partial P}\Big|_{\cancel{P}V}$$

everything is correct except the constants...

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$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$\frac{\partial S}{\partial V} \cancel{=} \frac{\partial P}{\partial T}$$

$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$\frac{\partial S}{\partial P} = \frac{\partial V}{\partial T}$$

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)$$

$$\Rightarrow \frac{\partial}{\partial P}(-S)\Big|_T = \frac{\partial}{\partial T}(V)\Big|_P \quad \Rightarrow \quad \frac{\partial S}{\partial P}\Big|_T = -\frac{\partial V}{\partial T}\Big|_P$$ yes!!

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Prob 5.17 $H = \frac{NI}{L}$ $H = \frac{B}{\mu_0} - \frac{M}{V}$

(a) $dH = \frac{N}{L} dI$

$dH = \frac{dB}{\mu_0} - \frac{dM}{V}$

?

$\nabla \cdot D = \rho$ ·

$\nabla \cdot H = 0$ ·

$\nabla \times D = \frac{\partial H}{\partial t}$ ·

$\nabla \times H = J + \frac{\partial D}{dt}$

(b) $W_{total} = VH\,dB$

$= VH$

$dH = \frac{dB}{\mu_0} - \frac{dM}{V}$

$\Rightarrow dB = \mu_0\left(dH + \frac{dM}{V}\right)$

$W_{total} = VH\mu_0\left(dH + \frac{dM}{V}\right)$

$= VH\mu_0 dH + H\mu_0 dM$

$= V\mu_0 d\left(\frac{H^2}{2}\right) + H\mu_0 dM$

$W_{total} - V\mu_0 d\left(H^2/2\right) = H\mu_0 dM$

(c) ?

(d) By subtracting of the self inductance ... ?

(8.18) I would imagine that a ~~big~~ large portion of the bricks potential → kinetic energy would be transformed into the thermal motion of the atoms that make up the brick + the earth. The energy has be distributed from many molecules moving in uniform ~~[illegible]~~ motion to many molecules moving in random arrangments.

(8.19) $F = U - TS$?

(8.20) ~~U~~$=$

$$S = k \ln 4 = (1.38 \cdot 10^{-23}\ \text{J/K}) \ln 4 = 1.913 \cdot 10^{-23}\ \text{J/K}$$

$$F = 10.2 \cdot (1.602 \cdot 10^{-19}\ \text{J}) - T(1.913 \cdot 10^{-23}\ \text{J/K}) > 0$$

$$10.2(1.602 \cdot 10^{-19}) > (1.913 \cdot 10^{-23})T$$ its positive

$$T < 8.54 \cdot 10^{4}\ \text{K}$$

(5.21)

G is extensive

$c = \frac{G}{m}$ is intensive

(5.22) eq 5.40 $\mu(T,P) = \mu^0(T) + kT\ln(P/P^0)$

The formula's in section 3.5

$$\mu = -T\frac{\partial S}{\partial N}\Big|_{U,V} \quad \& \quad \mu = \frac{\partial U}{\partial N}\Big|_{S,V}$$

For an ideal gas $S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$

$$\frac{\partial S}{\partial N} = \frac{S}{N} + Nk\left[\frac{1}{\left(\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right)}\left[\left(\frac{-V}{N^2}\right)\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2} + \frac{V}{N}\cdot\frac{3}{2}\left(\frac{4\pi m U}{3Nh^2}\right)^{1/2}\cdot\left(\frac{4\pi m U}{3N^2h^2}\right)(-1)\right]\right]$$

$$= \frac{S}{N} + Nk\left[(-1/N) + \frac{3/2(-1/N)}{(1)}\right]$$

$$= \frac{S}{N} + Nk\left[\frac{5}{2}\frac{1}{N}\right] = \frac{S}{N} + \frac{5}{2}k \quad \ldots$$

<u>10-16-02</u>

In section 3,5 we derived

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]$$ for a monatomic ideal gas

$PV = kNT$

$kT = \frac{PV}{N}$

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi m \cancel{k}}{h^2}\frac{PV}{N}\right)^{3/2}\right]$$

? This does not look like what we are looking for.

(5.23) $\Phi \equiv U - TS - \mu N$

$H = U + PV$

$F = U - TS$

$G = U + PV - TS$

(a) $d\Phi = dU - dT\cdot S - T\cancel{dS} - d\mu\cdot N - \mu\cancel{dN}$

$\quad\quad \| $

$\quad\quad T\cancel{dS} - p\,dV + \mu\cancel{dN}$

$= -p\,dV - S\,dT - N\,d\mu$

$$\Rightarrow \quad p = -\left.\frac{\partial\Phi}{\partial V}\right|_{T,\mu} \qquad S = -\left.\frac{\partial\Phi}{\partial T}\right|_{V,\mu} \qquad N = -\left.\frac{\partial\Phi}{\partial\mu}\right|_{V,T}$$

(b) $\cancel{dS}_{reservoir} = \cancel{+\frac{1}{T_R} dU_R}$

$$dU = TdS - PdV + \mu dN$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

For reservoir $dS = \frac{dU_r}{T} - \frac{\mu}{T} dN_r$

exchanging particles & energy but not volume $= -\frac{dU}{T} + \frac{\mu}{T} dN$

Now change in reservoirs' entropy is expressed in terms of systems variables

$$dS_{total} = dS_{system} + dS_{reservoir}$$

$$= dS +^{-} \frac{dU}{T} + \frac{\mu}{T} dN$$

$$= -\frac{1}{T}(-TdS + dU - \mu dN)$$

$$= -\frac{1}{T}(dU - TdS - \mu dN) > 0$$

= if $d\Phi = dU - TdS - \mu dN$ then Φ would have to decrease.
?

(c) ?

$\mu = ?$

$\Phi_1 = -13.6\,eV - (8800\,k)\cdot 0 -$

$\Phi_2 = 0 - (\quad)\cdot 0$

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(5.24) C(graphite) $\Delta_f G = 0$ kJ

C(diamond) $\Delta_f G = 2.9$ kJ / mole

$\therefore$ graphite is stabler at s.t.p

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \qquad dG = -S\,dT + V\,dP + \sum_i \mu_i\, dN_i$$

C(graphite) $V = 5.30\ \text{cm}^3 > V_{diam}$

C(diamond) $V = 3.42\ \text{cm}^3$

Assuming V constant $1\,\text{cm}^3 = 10^{-6}\,\text{m}^3$

$$G = V \cdot P + G_0$$

~~$G_{graphite}(P) =$ [illegible] $(10^{-6}\,\text{m}^3)P + 0$~~

~~$G_{diamond}(P)$~~ =

$$G_{graphite}(P) = (5.3(10^{-6})\,\text{m}^3)P + 0$$

$$G_{diamond}(P) = (3.42(10^{-6})\,\text{m}^3)P + 2900\ \text{J}$$

$$(5.3 - 3.42)10^{-6}\,P = 2900\ \text{J}/\text{m}^3$$

$\rightarrow P = 1.5 \cdot 10^9$ Pa $1\ \text{bar} = 10^5$ Pa

$= 15$ kilobars $1\ \text{kilobar} = 10^8$ Pa

(5.25) $\frac{kJ}{kbar} = \frac{10^3\ J}{10^3\ bar} = \frac{1\ N\cdot m}{10^5\ N/m^2} = 10^{-5}\ m^3$

(5.26) C(graphite) $S = 5.74\ J/K$

C(diamond) $S = 2.38\ J/K$

this entropy is at 1atm, T= 273 K + [illegible] implys that graphite would be the more stable form under these conditions.

Would the entropy change w/ pressure such that at a higher pressure the entropies switch values (which one is greater?)

?

(5.27) (a) $\left(\kappa \equiv -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T\right) \Rightarrow \frac{\partial V}{\partial P}\Big|_T = -V\kappa$

$$\frac{\partial G}{\partial P}\Big|_{T,N} = V \cong V_0 + \frac{\partial V}{\partial P}\Big|_T (V - V_0)$$

$$= V_0 - V_0\kappa_0(V - V_0) \pm \text{[illegible]}$$

$$= V_0 + V_0\kappa_0(V_0 - V) > V_0$$

→ Thus the slope of Graphite is <u>steeper</u> than originally predicted

∴ transformation pressure should happen at a <u>lower</u> pressure.

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(b) $\kappa_{\text{graphite}} = 3\cdot 10^{-6}\ \text{bar}^{-1}$ ⇒ ∀ atmosphere of pressure increase graphite shrinks by 3 one millionth.

$$\equiv$$

$$-\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T = \kappa \text{ const.} \Rightarrow$$

$$\frac{\partial V}{\partial P}\Big|_T = -V\kappa$$

$$\frac{\partial G}{\partial P}\Big|_{T,N} = V \qquad = V(P,T_0) = -V\kappa P$$

$$= -V\kappa P$$

$$\Rightarrow G \cong \int^{P} -V_0\kappa_0 P'\,dP' = -V_0\kappa_0\frac{P^2}{2} + G_0$$ equate & solve...

		ΔH_f	$\Delta_f G$ (kJ)	S	C_p	V (cm^3)
⑤.28	$CaCO_3$ (calcite)	−1206.9	−1128.8	92.9	81.88	36.93
	$CaCO_3$ (aragonite)	−1207.1	−1127.8	88.7	81.25	34.15

(a) Arguing that the form w/ the smallest Gibbs free energy is the stablest form gives calcite as the stable form.

(b) ~~Again~~ as $\frac{\partial G}{\partial P}\Big|_{T,N} = V$ Assuming the volume does not change w/ P. i.e. the compressibility is negligible over the range of pressures considered ...

$$G = VP + G_0.$$

$$G_{\text{calcite}} = (36.93\cdot 10^{-6}\,\text{m}^3)P + -1128.8\text{ kJ}$$

$$G_{\text{aragonite}} = (34.15\cdot 10^{-6}\,\text{m}^3)P + \ldots$$

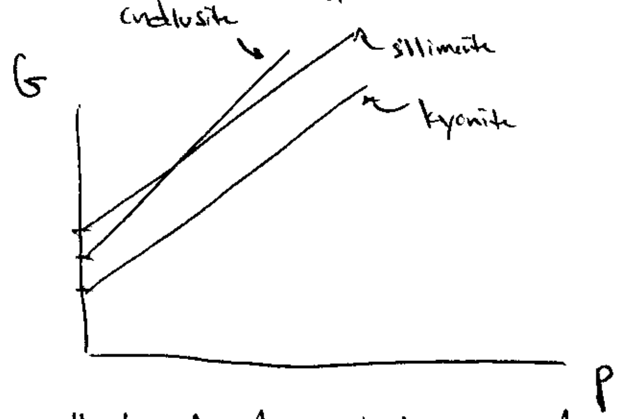
(5,29)

Al_2SiO_5	ΔH_f	$\Delta_f G$ (TS)	S (7K)	C_p	V
kyanite	-2594.29	-2443,88	83.81	121,71	44.09
andalusite	-2590,27	-2442,66	93.22	122,72	51,53
sillimenite	-2587,76	-2440.99	96,11	124,52	49,90

(a) The phase w/ the lowest gibbs free energy is the stablest form

⇒ kyanite

$$\frac{\partial G}{\partial P}\bigg|_{V,T} = V$$



Then kyanite starts as the smallest & stays that way for all pressures.

(b) $dG = -S\,dT + V\,dP + \sum_i \mu_i\, dN$

$$\frac{\partial G}{\partial T}\bigg|_{P,N} = -S$$

$$\Rightarrow G(T_2) - G(T_1) = -\int_{T_1}^{T_2} S(T)\,dT$$

(c) $\Delta G(T_2) = \Delta G(T_1) - \Delta S(T_1)(T_2 - T_1)$

$$\Delta G_{kyanite}(T) = -2443{,}88 - 83{,}81(T-273)$$

$$\Delta G_{andalusite}(T) = -2442{,}66 - 93{,}22(T-273)$$

$$\Delta G_{\text{sillimanite}} = -2440. - 96.11(T-273)$$

stablest form is the one w/ ΔG smallest.

(d) $\left.\frac{\partial S}{\partial T}\right|_V = \frac{C_V}{T}$

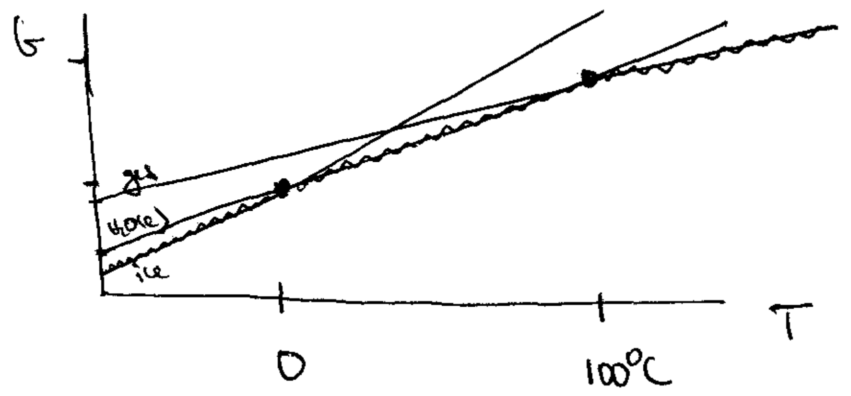
$$\left.\frac{\partial S}{\partial T}\right|_P = \frac{C_P}{T}$$

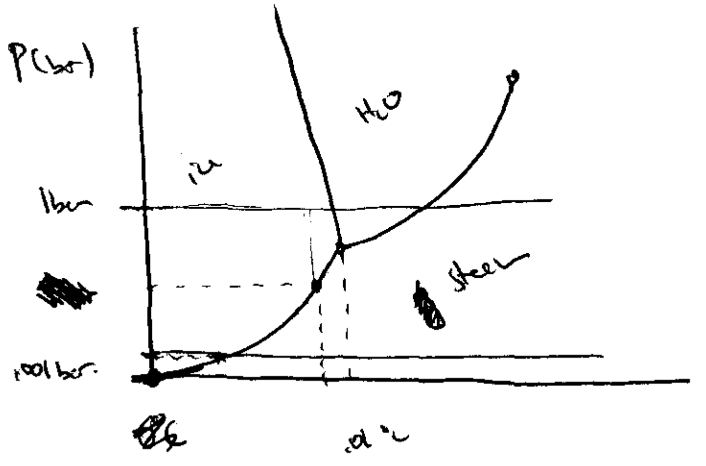
$$\left.\frac{\partial S}{\partial T}\right|_P \cong \frac{120\text{ kJ}}{T}$$

don't know how to comment on the validity of constant entropy approximation.

(8.30)

ice ⟶ $H_2O(l)$ ⟶ gas





At .001 bar the temperatures [illegible] there would be no liquid phase.

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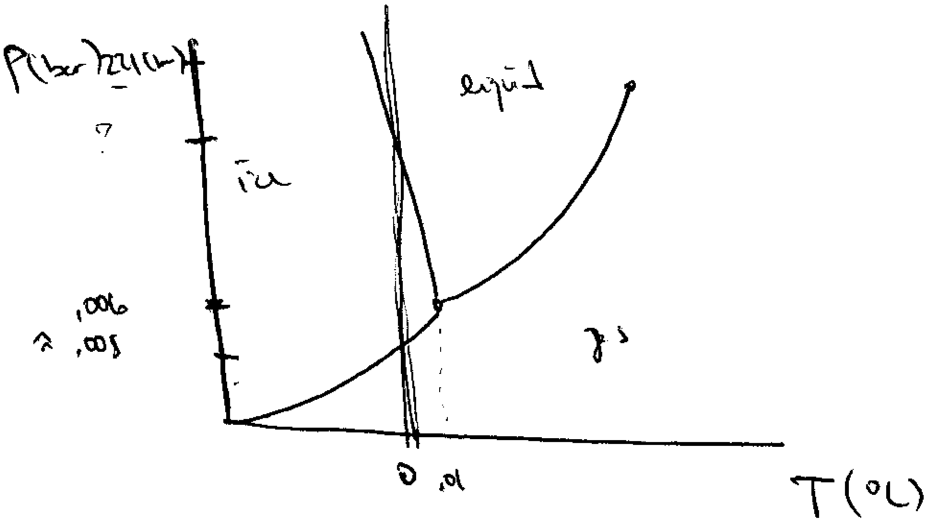
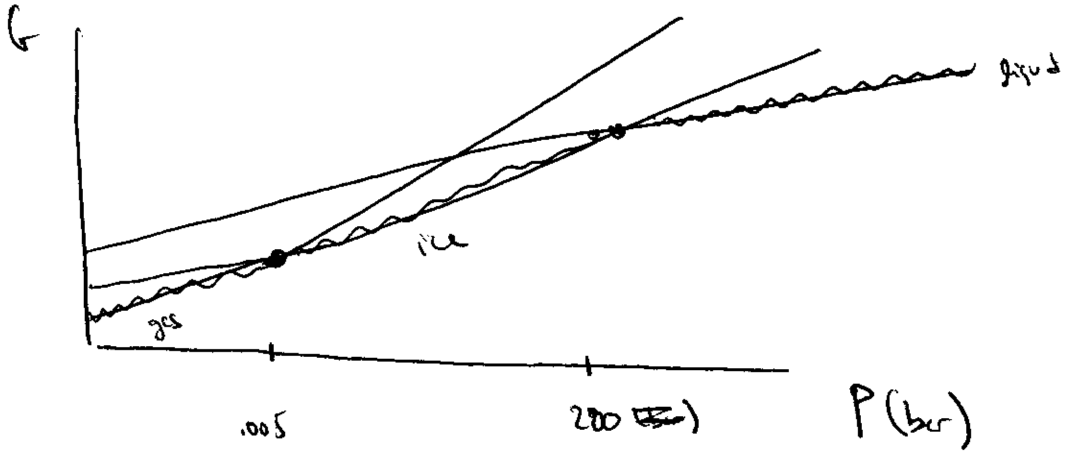
(5.31)



At high temp. there might be no ice phase



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(5.32)

$\frac{dP}{dT} = \frac{L}{T\Delta V}$ per mole

$\rho_{ice} = 917\ kg/m^3$

$\rho_{H_2O} = 1\ g/cm^3$

$= 10^{-3}\ kg / 10^{-6}\ m^3 = 1000\ kg/m^3$

Change /mole into /kg

$L_{ice \to H_2O} = 333\ J/g$

$1\ mole = M\ kg$ M = molecular weight in kg's.

$\frac{x}{mole} = \frac{x}{1\ kg} \cdot \frac{M\ kg}{1\ mole}$

$\Delta S = \frac{L}{T}$

$\frac{dP}{dT} = \frac{S_s - S_\ell}{V_s - V_\ell}$

$= \frac{L}{T(V_s - V_\ell)}$

$\Leftrightarrow \frac{dP}{dT} = \frac{L}{T\Delta(\rho^{-1})}$ per kg

$=$

$= \frac{L}{T\left(\frac{1}{\rho_s} - \frac{1}{\rho_\ell}\right)}$

$= \frac{L}{T}\frac{1}{\left(\frac{1}{917} - \frac{1}{1000}\right)} = \frac{L}{T}(1.1 \cdot 10^4)\ kg/m^3$

... I know $S_s < S_\ell \Rightarrow S_s - S_\ell = -\frac{L}{T}$ ← w/ minus sign

& ∴ $\frac{dP}{dT} = -\frac{L}{T}(1.1 \cdot 10^4\ kg/m^3)$

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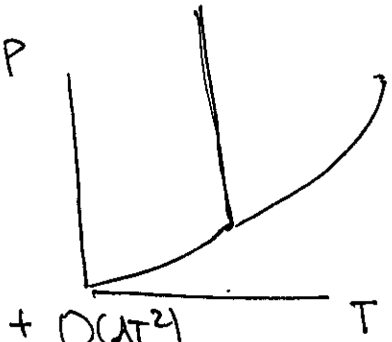
(b) $$\frac{dP}{dT} \cong -\frac{333\ \mathrm{J/kg}\cdot 10^3}{(273\ \mathrm{K})}\left(1.1\cdot 10^4\ \mathrm{kg/m^3}\right)$$

$$= \begin{matrix} -1.341\cdot 10^7\ \mathrm{Pa/K} \\ \cancel{1.34\cdot 10^4}\ \cancel{\mathrm{Pa/K}} \end{matrix} = -132.4\ \mathrm{atm/K}$$



At P = 1 atm. T = 0°C.

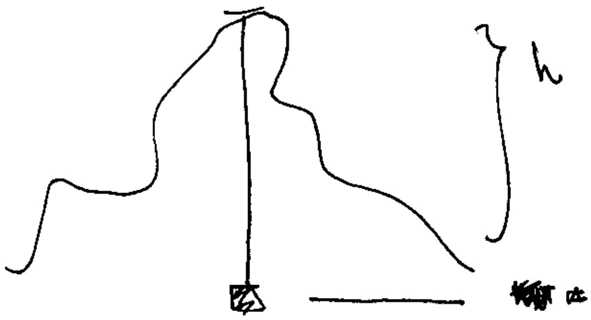
$$P(-1°\mathrm{C}) \cong P(0°\mathrm{C}) + \left.\frac{dP}{dT}\right|_{0°\mathrm{C}}\cdot(-1-0) + O(\Delta T^2)$$

$$= 1\ \mathrm{atm} + (132.4\ \mathrm{atm})(+1)$$

$$= \cancel{131.4}\ \cancel{\mathrm{atm}}\ 133.4\ \mathrm{atm}.$$

$$f(x+h) = f(x) + f'(x)h + O(h^2)$$
$$f(x) = f(x_0) + f'(x_0)(x-x_0) + O((x-x_0)^2)$$

(C) ~~Assume that the density~~ ~~is~~



$$\rho_{liq} h g = P = 133.4\ \mathrm{atm}$$

$$h = 1.5\ \mathrm{km}$$

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(d) 150 lbs = 68.1 kg = Mass of skater

Force = Mg

Area = (12 inch)(1 cm) = $30.48 \cdot 10^{-4}\ m^2$

$$P = \frac{(68.1)(9.8)}{30.48 \cdot 10^{-4}} = 2.19 \cdot 10^5\ \text{Pa} = 2.16\ \text{atm.}$$

$$\Delta P = 2.16\ \text{atm} - 1\ \text{atm} \cong \left.\frac{dP}{dT}\right|_{1\text{atm}} (\Delta T)$$

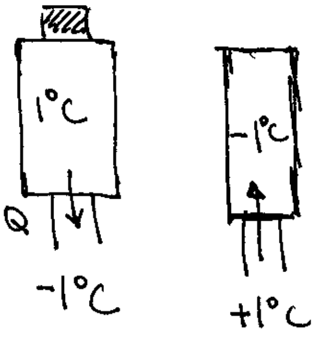
would give the change in melting temperature due to the additional weight

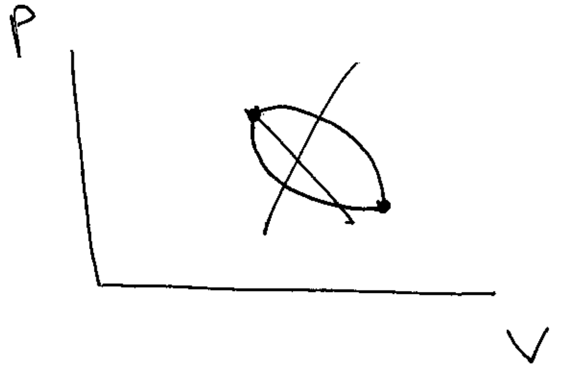
$$\left.\frac{dP}{dT}\right|_{1\text{atm}} = -132.4\ \text{atm}/\text{K}$$

$\Delta T = -8.76 \cdot 10^{-3}$ K a negligible change.

How do we know that the changes are not very, very slight?

5.33





$$e \equiv \frac{W}{Q_{in}} = \frac{\text{Work}}{Q_{removed}}$$

Clausius-Clapeyron relation:

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

The device has to absorb a finite amount of heat because upon

freezing, $L_{ice \to liqui}$

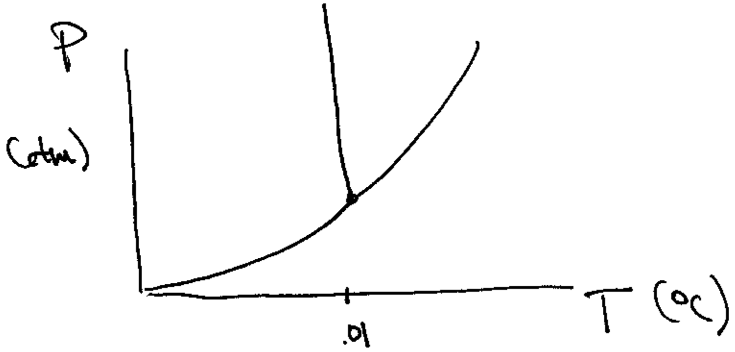
For H_2O

$L_{solid \to liquid}$

$L_{sl} = +333\ J/g$ $L_{lg} = +2260\ J/g$

The machine has to remove 333 J/g of heat

~~while on melting~~



(1) w/ weight on the amount of [illegible] heat that must be ~~added~~ removed is .

i) enough to bring the system from 1°C to the freezing point.

ii) To freeze the liquid H_2O.

iii) To bring the liquid from the freezing point to $-1°C$

(2) The amount of work done by the system under these conditions is (ignoring the expansion of the liquid & solid when not changing state

$\Leftrightarrow \beta \equiv \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p \ll 1$ i.e. the termal)

$$W = p \cdot \Delta V_{ls} = \frac{Mg}{A_{piston}} \cdot \Delta V_{ls},$$

(3) The ...

Assume [illegible] the weight has mass m_w, & the mass of the working substance [illegible] m_{H_2O}.

$$-Q_{removed} = c_p m_{H_2O}(T_f - 274) + c_p m_{H_2O}$$

$$= c_p m_{H_2O}(T_f^* - T_{0i}) + [illegible] \; m_{H_2O}L + c_p m_{H_2O}(T_f - T^*)$$

$$W = m_w g$$

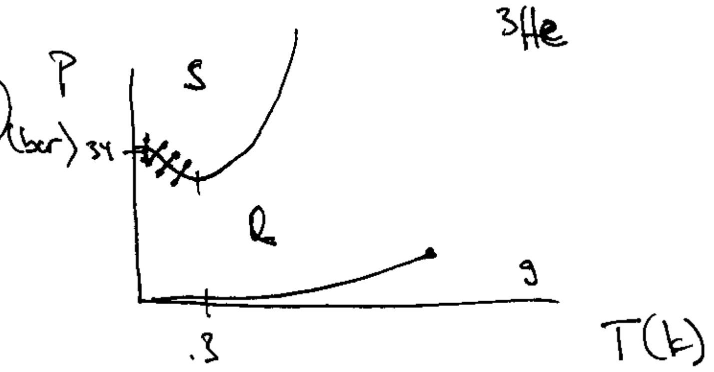
? Don't -

~~$\ell =$~~

$$e = \frac{P_0 \Delta V}{m_{H_2O} \cdot L} = \frac{P_0}{m_{H_2O}}\left(\frac{\Delta V}{L}\right) = \frac{P_0}{m_{H_2O}} \cdot \frac{dT}{T\,dP}$$

Don't see how to do this problem?

S, 34



$$\frac{dP}{dT} < 0$$

(a) $\frac{dP}{dT} = \frac{L}{T\Delta V} < 0 \quad \rightarrow \quad \Delta V < 0$

$\Delta V \equiv V_\ell - V_s < 0$

$$\frac{L}{T} = S_\ell - S_s$$

$V_\ell < V_s \quad \therefore$ liquid is <u>more dense</u>

I as assuming that the liquid phase has more entropy.

(b) $\frac{dP}{dT} = \frac{S_s - S_\ell}{V_s - V_\ell}$

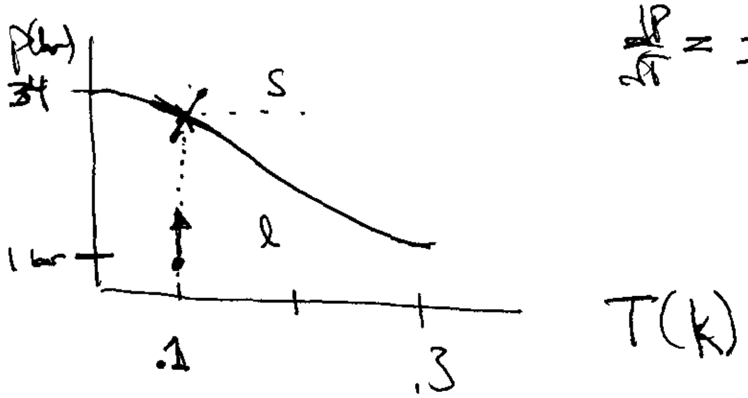
As $T \to 0$.

$S_s = S_s(T) \to 0$
$S_\ell = S_\ell(T) \to 0$ } By 3rd law of thermodynamics

$\therefore \quad S_s - S_\ell \to 0$

$\& \quad \frac{dP}{dT} \to 0.$

(c)



$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

Adiabatic compression ⇒ no heat change + $\Leftrightarrow$ $dS = 0$.

$$\therefore \quad \frac{dP}{dT} \cong \frac{\Delta S}{\Delta V} = \qquad\qquad dS = \frac{dQ}{T}$$

$$\frac{dP}{dT} = \frac{S_s - S_0}{\Delta V} < 0$$

w/ S_0 = entropy at room temp + pressure.

Since we require the phase change to also take place adiabatically it will have to not involve changing the entropy from S_0. ⇒ $\frac{dP}{dT} \cong 0$. Since the only place on the phase diagram where this happens is at $T = 0$ the system should move towards that state i.e. The temperature will <u>decrease</u>.

5.35

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

$$= \frac{L(T,P)}{T\Delta V(T,P)}$$

$$\cong \frac{L}{T\,\cancel{\Delta V}\,V_{gas}} \qquad L \text{ constant}$$

$\Delta V = V_f - V_i$

$= V_{gas}$

$$V = \frac{NkT}{P} = \frac{nRT}{P}$$

$$\Rightarrow \quad \frac{dP}{dT} = \frac{L}{T\left(\frac{NkT}{P}\right)} = \frac{L}{T\left(\frac{nRT}{P}\right)} = \frac{PL}{nRT^2}$$

$$\Rightarrow \quad \frac{dP}{P} = \frac{dT}{T^2}\left(\frac{L}{nR}\right)$$

$$\ln P = -\frac{1}{T}\left(\frac{L}{nR}\right) + C \quad \Rightarrow \quad P = C_0 \exp\left\{-\frac{L}{nRT}\right\}$$

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5.36

$T = 50°C \Rightarrow T = 50 + 273 = 323 K$

$T = 100°C \Rightarrow T = 373 K$

From Fig 5.11. $L(kJ/mol) \cong \frac{1}{2}(42.92 + 40.66) = 41.790 \ kJ/mol$

$= $ [illegible]

$R = 8.314 \ J/mol \cdot K$

So $$P = C_0 \exp\left\{ \frac{-41.79 \cdot 10^3 \ J/mol}{(8.314 \ J/mol \cdot K) T} \right\}$$

$$\Rightarrow P = C_0 \exp\left\{ \right.$$

Fitting equation at the left end point:

$$0.1234 \ bar = C_0 \exp\left\{ \frac{-41.79 \cdot 10^3 \ J/mol}{(8.314 \ J/mol \cdot K)(323 K)} \right\}$$

$\Rightarrow C_0 = \ldots$

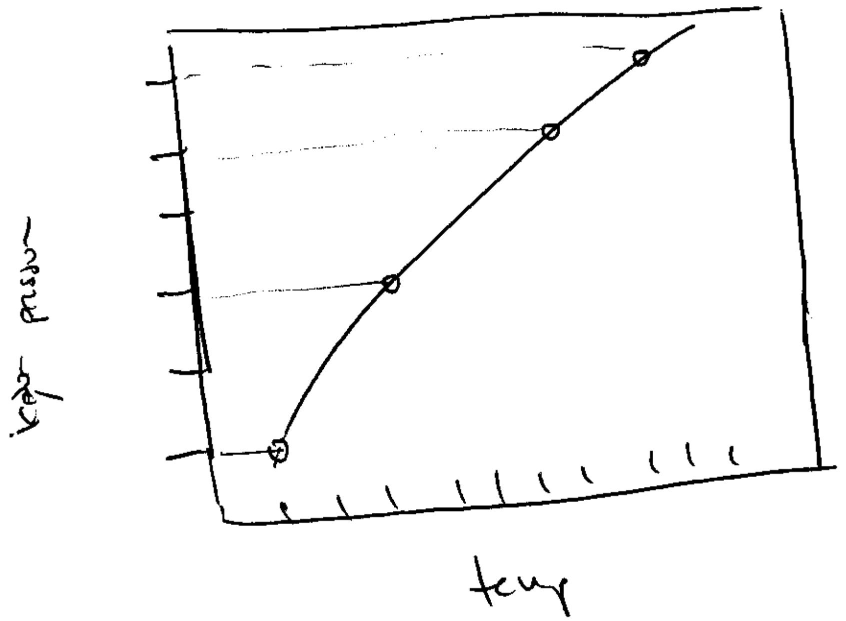
Then plot $P(T)$ for $T \in [323 K, 373 K]$

Prob 1.16 asks for pressures at given heights

& derives $P(z) = P_0 \exp\left\{\frac{-mg}{RT} z\right\}$

⇒ $P(z) = (1\,\mathrm{atm}) \exp\left\{ \underline{-z} \cdot 9.822 \cdot 10^{-5} \right\}$

& at heights = 4700 ft, 1430 m
10150 ft, 3090 m
14,500 ft, 4420 m
8850 m
} ⇒ P(height) =



As the height ↗ the atmospheric pressure ↘ & the temperature at which H_2O boils decreases

I would think this would mean that ~~the~~ it gets easier to cook in the mountains.

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5.37

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$ By Clausius Clapeyron

$V_{calcite} = 36.93\ cm^3$ → $\Delta V = 2.78\ cm^3$

$V_{aragonite} = 34.15\ cm^3$

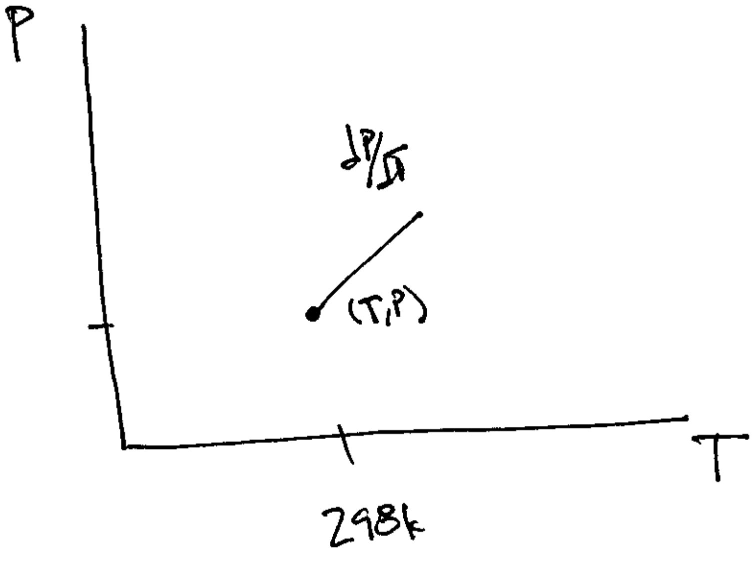
$T = 298\ k$

$L = \cancel{\frac{\Delta S}{T}}$ $\Delta S = \frac{L}{T}$ → $L = T\Delta S$

∴ [illegible] = S_{cal} = . . . ΔS = . . .

S_{ara} = . . .

$$\frac{dP}{dT} = \frac{T\Delta S}{T\Delta V} = \frac{\Delta S}{\Delta V}$$



5.38

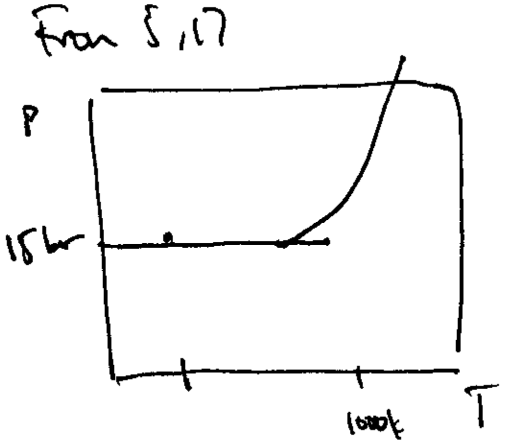
ΔS = . . .

$L = T\Delta S$

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{T\Delta S}{T\Delta V} = \frac{\Delta S}{\Delta V} = ..20$$

↑ predicted by graph.

From 5.17



For low temp: $\Delta S \approx 0$ between the graphite phase + the diamond phase

+ At high temp $\Delta S \propto \Delta V$

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Prob 5.39

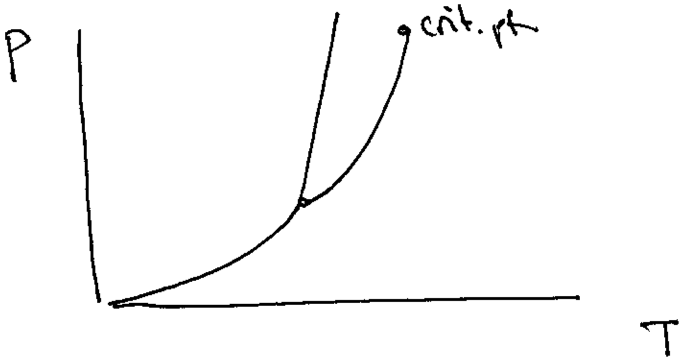
By Clausius Clapeyron Eq

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

w/ $L = T\Delta S$

$$\therefore \frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

"typical" phase diagrams look like



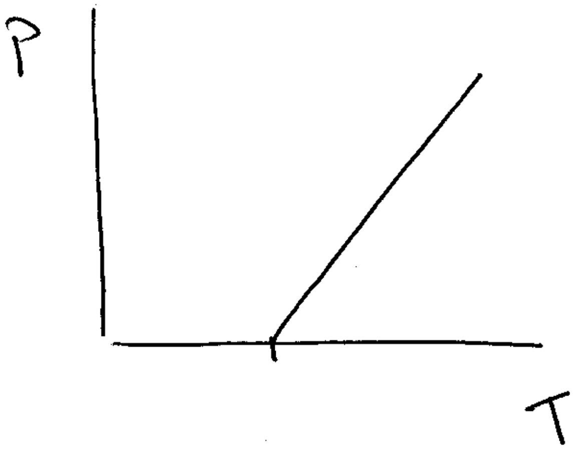
5.40

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$ ~~[illegible]~~ Assumed independent of T & P. at S.T.P.

$$= \frac{((133.5+41.84) - 207.4)\ \text{J/K}}{((60.4+22.69) - 100.07)\ \text{cm}^3} = 1.88\ \text{J/cm}^3\cdot\text{K}$$

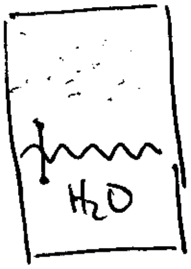
$$\rightarrow \quad P - P_0 = \left(\frac{\Delta S}{\Delta V}\right)_0 (T - T_0)$$

→ P



5.41

initially → pump gas into top.



diffusion of particles occurs across this surface

∴ Chemical potentials must change to match each other

$$d\mu_l = d\mu_g$$

eg 5.40 $\mu(T,P) = \mu^0(T) + kT\ln(P/P^0)$ chem potential of ideal gas.

$$d\mu_l = d\left(\mu^0(T) + kT\ln(P/P^0)\right)$$

$$? = \frac{kT}{P_v}$$

vapor pressure

Assuming $P_v(P) = P_v(P_v)\, e^{(P-P_v)V/NkT}$

25° C ≈ $P_v(P_v) = 1$ atm.

$PV = NkT$

$$?\ \left(\frac{V}{NkT}\right) \approx \cancel{\frac{V}{10^{23}(1.38\cdot 10^{-23})}}$$

$$\frac{\cancel{V}\ (1\ \text{liter})}{(6.022\cdot 10^{23})(1.38\cdot 10^{-23}\ J/K)(300\ K)}$$

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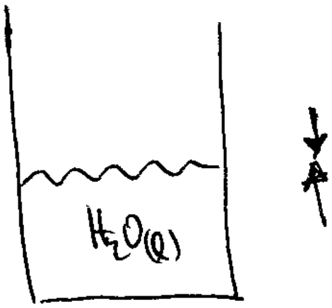
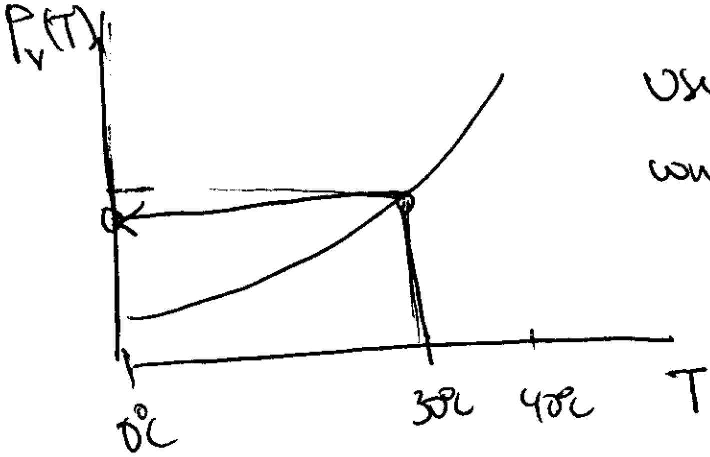
5.42



rel Humidity $= \dfrac{PP_{H_2O}}{P_v(}$

$P_v = P_0 e^{-L/RT}$ (vapor pressure eq.)

Fig 5.11 gives $\{L_i\}, \{T_i\}, \{P_{v_i}\}$



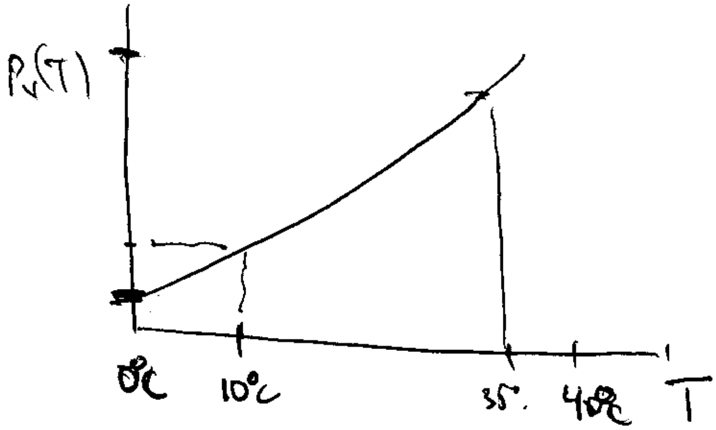
Use to get $P_v(30°C)$ then compute PP_{H_2O} having rel Hum = 90%
= 40%.

(5.43) rel Hum = .9

$$35^\circ C \Longrightarrow \quad 10^\circ C$$

rel Hum = .9 | rel Hum = ?

Since we can see our breath ⇒



$$\text{rel Hum} \equiv \frac{PP_{H_2O}}{P_v(T)}$$

$$\parallel$$

$$.9 = \frac{PP_{H_2O}}{P_v(35^\circ C)}$$

← read from graph in prob. 5.42

⇒ $PP_{H_2O} = \ldots$

Then relative Humidity $\equiv \dfrac{PP_{H_2O}}{P_v(10^\circ C)} = \ldots$

(5.44) $z = ?$

$T(z) = 25^\circ C + -10^\circ C (z)$

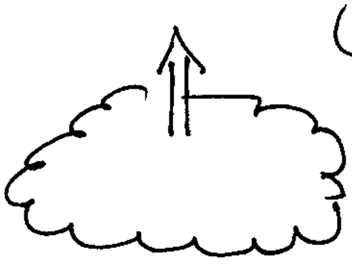
$$\frac{dT}{dP} = \frac{2}{f+2}\frac{T}{P}$$

$$\frac{dT}{dz}\cdot\frac{dz}{dP} = \frac{2}{f+2}\cdot\frac{T}{P}$$

$$\frac{dT}{dz} = \left(\frac{dP}{dz}\right)\cdot\frac{2}{f+2}\frac{T}{P}$$

$$\frac{dT}{dz} = -10\,^\circ C/\text{km}$$

dry adiabatic lapse rate.



$z = 0$

$T = 25^\circ C$

rel Hum = .5

$$\equiv \frac{PP_{H_2O}}{P_v(25^\circ C)} = .5$$

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Assuming I have a graph of $P_v(T)$.

Then I compute $PP_{H_2O} = \cdots$

Require

$$\frac{PP_{H_2O}}{P_v(25-10z)} \overset{?}{=} 1$$

solve for z.

5.45

$$\left(\frac{7}{f+2}\right)\frac{T}{P}\,dP$$

(a) From

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

$$\cong \frac{L}{TV_g}$$

$$PV = kNT$$

Adiabatic expansion w/ phase change...

?

$$dT = \frac{2}{7}\frac{T}{P}\,dP - \frac{2}{7}\frac{L}{nR}\,dn_w$$

(b)

$$\frac{n_w}{n} = F(T,P)$$

$$\frac{dn_w}{n} = \left.\frac{\partial F}{\partial T}\right|_P dT + \left.\frac{\partial F}{\partial P}\right|_T dP$$

$$\cancel{dT = \left(\frac{2}{7}\frac{T}{P} + \frac{\partial F}{\partial P}\Big|_T\right) dP - \frac{2}{7}\frac{L}{R}}$$

$$dT = \frac{2}{7}\frac{T}{P}\,dP - \frac{2}{7}\frac{L}{R}\frac{\partial F}{\partial T}\Big|_P dT - \frac{2}{7}\frac{L}{R}\frac{\partial F}{\partial P}\Big|_T dP$$

$\Rightarrow$

$$\left(1 + \frac{2}{7}\frac{L}{R}\frac{\partial F}{\partial T}\Big|_P\right) dT = \left(\frac{2}{7}\frac{T}{P} - \frac{2}{7}\frac{L}{R}\frac{\partial F}{\partial P}\Big|_T\right) dP$$

?

$\boxed{5.46}$ $\sigma = \dfrac{G_{\text{bndr}}}{A}$ $\sigma = 0.073\ J/m^3$

(a)

$$G = N_\ell \mu_\ell + (N - N_\ell)\mu_v$$

At eq $\mu_\ell = \mu_v \equiv \mu$

$\therefore G = N\mu$

$$N_\ell = \frac{\left(\frac{4}{3}\pi r^3\right)}{v_\ell}$$

$$\therefore G = \frac{\left(\frac{4}{3}\pi r^3\right)}{v_\ell}\mu_\ell + \left(N - \frac{\frac{4}{3}\pi r^3}{v_\ell}\right)\mu_v$$

$$G = \left(\frac{\frac{4}{3}\pi r^3}{v_\ell}\right)\mu_\ell + \left(N - \frac{\frac{4}{3}\pi r^3}{v_\ell}\right)\mu_v$$

$$+ (4\pi r^2)\sigma$$

(c) ? Thought $\mu_\ell = \mu_v$?

(d) ?

(5.47) $dG_M = -S\,dT - \mu_0 M\,dH$

$= -S\,dT - M(\mu_0\,dH)$

At a phase boundary ~~$dG_M = 0$~~ $\Delta G_{M\,total} = 0$

$\Rightarrow \quad dG_1 = dG_2$

$\Rightarrow -S_1\,dT - M_1(\mu_0\,dH) = -S_2\,dT - M_2(\mu_0\,dH)$

$\Rightarrow \cancel{\frac{dT}{\mu_0\,dH}} = \frac{\cancel{-(S_1 - S_2)}}{M_1 - M_2} = \frac{-(L)}{T\Delta M}$

$dT(-S_1 + S_2) = (M_1 - M_2)(\mu_0\,dH)$

$\frac{dT}{(\mu_0\,dH)} = \cancel{-(S_1+S_2)} \quad \cancel{M_1 M_2} \quad \left(\frac{M_1 - M_2}{-S_1 + S_2}\right)$

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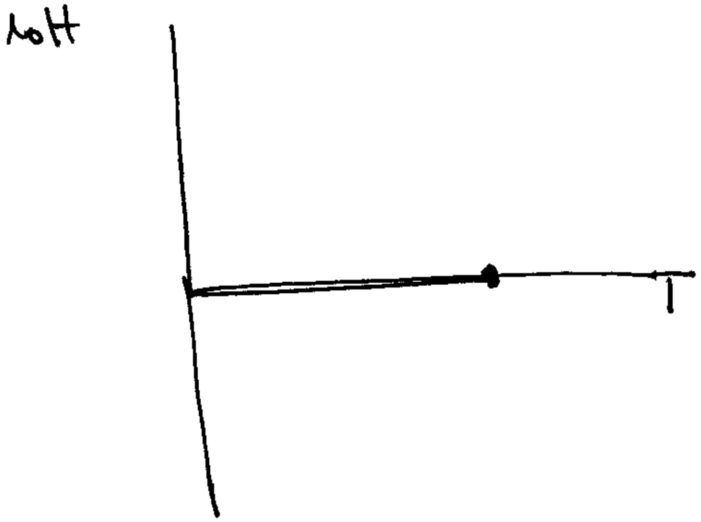
$$\therefore \quad \frac{dT}{\mu_0 dH} = -\frac{(M_1 - M_2)}{(S_1 - S_2)}$$

$$\Rightarrow \quad \frac{\mu_0 dH}{dT} = -\frac{L}{T \Delta M}$$



(b) ?

(c) ?

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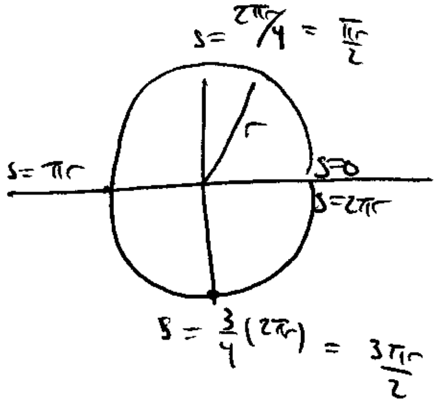
Prob A.20



$\psi = \psi(s)$

p well defined.

Sin

?

Prob A.21

$$|\vec{L}|^2 = \ell(\ell+1)\hbar^2 \qquad \ell = 1, 2, 3, \ldots$$

$$E = \frac{-2\pi^2 m_e e^4 k_e^2}{h^2}\frac{1}{n^2} \qquad n = 1, 2, 3,$$

$$L_z = m\hbar \qquad -\ell \le m \le \ell$$

$n = 1$

$\ell = 1,$ [illegible] $\ldots$ $\qquad \ell = 2$ $\qquad$?

$m = -1, 0, +1$ $\qquad m = -2, -1, 0, +1, +2$

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(5.48)

$$P(V) = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}$$

(1) $$\frac{dP}{dV} = \frac{(-1)NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3} = 0$$ see.

(2) $$\frac{d^2P}{dV^2} = \frac{2NkT}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0$$ don't see

From eq (1) $$NkT = \frac{2aN^2}{V^3}(V-Nb)^2$$

So from eq (2)

$$\frac{2}{(V-Nb)^3} \cdot \frac{2\cancel{aN^2}}{\cancel{V^3}}(V-Nb)^2 - \frac{6\cancel{aN^2}}{V^4} = 0$$

$$\frac{4}{(V-Nb)} - \frac{6}{V} = 0$$

$$2V - 3(V-Nb) = 0$$

$$2V - 3V + 3Nb = 0$$

$$-V + 3Nb = 0 \qquad \underline{\underline{V_c = 3Nb}}$$

Then From (1) $$(-1)\frac{\cancel{N}kT}{(3Nb-Nb)^2} + \frac{2aN^{\cancel{2}}}{(3Nb)^3} = 0$$

$$\Rightarrow \quad \frac{-kT}{4\cancel{N^2}b^2} + \frac{2a\cancel{N}}{27N^3b^3} = 0$$

$$\Rightarrow \quad T = \frac{8(1)a}{27bk} \quad \checkmark$$

Then $$P_c = \frac{N\left(\frac{8a}{27b}\right)}{(3Nb - Nb)} - \frac{aN^2}{(9N^2b^2)}$$

$$= \frac{8aN}{27b}\frac{1}{(2Nb)} - \frac{a}{9b^2}$$

$$= \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{4a - 3a}{27b^2} = \frac{a}{27b^2} \quad \checkmark$$

5.49

	$N_2: a = 4\cdot10^{-49}\,J\cdot m^3,\ b = 6\cdot10^{-29}\,m^3$	$H_2O: a = 16\cdot10^{-49}\,J\cdot m^3,\ b = 6\cdot10^{-29}\,m^3$
V_c/N		
P_c		
kT_c		

	$He: a = \frac{1}{40}\cdot4\cdot10^{-49}\,J\cdot m^3,\ b = ?$
V_c/N	
P_c	
kT_c	

$\boxed{8.50}$ $$\frac{PV}{NkT} = \frac{V}{V-Nb} - \frac{aN^2}{V(NkT)}$$ For van der walls gas.

(*) $$\frac{PV}{NkT} = \frac{V}{V-Nb} - \frac{aN}{VkT}$$

$$= \frac{1}{1-\frac{Nb}{V}} - \frac{aN}{VkT}$$

$$\left\{ \frac{1}{1-x} = \sum_{k=0}^{\infty} x^k \right\}$$

$$= 1 + \frac{Nb}{V} + \frac{N^2b^2}{V^2} + \frac{N^3b^3}{V^3} + \cdots$$

$$-\frac{aN}{VkT}$$

$$= 1 + \frac{N}{V}\left(b - \frac{a}{kT}\right) + \frac{N^2b^2}{V^2} + \frac{N^3b^3}{V^3} + \cdots$$

\- - —

From eq (*) At critical point

$$\frac{P_cV_c}{NkT_c} = \frac{3Nb}{2Nb} - \frac{a\cancel{N}}{(3\cancel{N}\cancel{b})\cancel{k}\left(\frac{8}{27}\frac{\cancel{a}}{\cancel{b}}\right)}$$

$$= \frac{3}{2} - \frac{9}{8} = \frac{3}{12} = \frac{1}{4}$$ <u>independent</u> of a or b.

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(5.51) $V_c = 3Nb \;;\; P_c = \frac{1}{27}\frac{a}{b^2} \;;\; kT_c = \frac{8}{27}\frac{a}{b}$

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

let $t = \frac{T}{T_0} \;;\; v = \frac{V}{V_0} \;;\; p = \frac{P}{P_0}$

$$\Rightarrow \left(pP_0 + \frac{aN^2}{V_0^2 v^2}\right)(V_0 v - Nb) = NkT_0 t$$

$$\Rightarrow t = \frac{P_0}{NkT_0}\left(p + \frac{aN^2}{V_0^2 P_0 v^2}\right)V_0\left(v - \frac{Nb}{V_0}\right) -$$

$$\Rightarrow t = \frac{P_0 V_0}{NkT_0}\left(p + \frac{aN^2}{V_0^2 P_0 v^2}\right)\left(v - \frac{Nb}{V_0}\right)$$

take $\underline{V_0 = Nb}$ & $\frac{aN^2}{V_0^2 P_0} = \frac{aN^2}{N^2 b^2 P_0} \overset{\text{set}}{=} 1 \; - \; \underline{P_0 = \frac{a}{b^2}}$

& then $\frac{P_0 V_0}{NkT_0} \overset{\text{set}}{=} 1$

$\frac{(a/b^2)(Nb)}{NkT_0} = 1 \Rightarrow \underline{kT_0 = \frac{a}{b}}$ & dimensionless eq becomes:

$t = \left(p + \frac{1}{v^2}\right)(v - 1)$

with regard to scaling let $V_0 = 3Nb$, $P_0 = \frac{1}{27}\frac{a}{b^2}$, $kT_0 = \frac{8}{27}\frac{a}{b}$

Then

$$t = \left(\frac{P_0 V_0}{NkT_0}\right)\left(P + \frac{aN^2}{V_0^2 P_0 v^2}\right)\left(v - \frac{Nb}{V_0}\right)$$

$$\Rightarrow t = \frac{\left(\frac{1}{27}\right)\left(\frac{a}{b^2}\right)(3\cancel{N}\cancel{b})}{\cancel{k}\cancel{N}\left(\frac{8}{27}\frac{a}{\cancel{b}}\right)}\left(p + \frac{a\cancel{N}^2}{9\cancel{N}^2 b^2\left(\frac{1}{27}\frac{a}{b^2}\right)v^2}\right)\left(v - \frac{\cancel{N}b}{3\cancel{N}b}\right)$$

$$= \frac{1}{9}\cdot\frac{27}{8}\left(p + \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right)$$

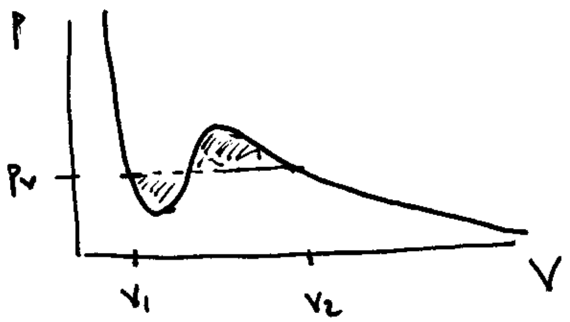
$$= \cancel{8}\ \frac{3}{8}\left(p + \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right)$$ independent of a + b !!

$\boxed{5.52}$ if $t = .95 = \frac{3}{8}\left(p + \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right)$

$$\Rightarrow \quad p = \frac{t}{\left(v - \frac{1}{3}\right)}\left(\frac{8}{3}\right) - \frac{3}{v^2}$$

$$p = \frac{8t}{(3v - 1)} - \frac{3}{v^2}$$

plotting... to be done ... assuming



$$0 = \int_{V_1}^{V_2} (P_v - p(v))\,dv$$

$$= P_v(V_2 - V_1) - \int_{V_1}^{V_2} p(v)\,dv$$

$$\Rightarrow \quad P_t = \frac{1}{V_2-V_1}\int_{V_1}^{V_2} p(v)\,dv \quad \ldots$$

$$= \frac{1}{V_2-V_1}\int_{V_1}^{V_2}\left(\frac{8t}{(3v-1)} - \frac{3}{v^2}\right) dv$$

$$= \frac{1}{V_2-V_1}\left[\frac{8t}{(3v-1)^2}\frac{1}{3} - \left(-\frac{3}{(-1)v}\right|_{V_1}^{V_2}$$

From 5.57 w/ $p = \frac{8t}{(3v-1)} - \frac{3}{v^2}$

$$0 = \int_{loop} V\,dP \qquad V = V(p)$$

$$\frac{dp}{dV} = \frac{8t(3)}{(3v-1)^2} - \frac{6}{V^3}$$

$$= \int_{loop} V\,\frac{dP}{dV}\cdot dV$$

$$0 = \int_{loop.}\left(\frac{24t\,V}{(3v-1)^2} - \frac{6}{v^2}\right) dv$$

How do I compute numerically the maxwell construction?

From 5.56:

$$G = -NkT\ln(V-Nb) + \frac{(NkT)(Nb)}{V-Nb} - \frac{2aN^2}{V} + c(T)$$

$$Nb = \frac{V_c}{3} \qquad \frac{G}{NkT} = -\ln\left(V-\frac{V_c}{3}\right) + \frac{V_c/3}{(V-V_c/3)} - \frac{2aN^2}{(NkT)V} + \frac{c(T)}{NkT}$$

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$$\frac{G}{NkT} = -\ln\left(v - \frac{v_c}{3}\right) + \frac{v_c/3}{\left(v - v_c/3\right)} - \underbrace{\frac{2aN}{kTV}}_{\text{How handle this term?}} + C'(T)$$

take $v_c = 1$

Don't understand?

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(5.54)

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$= T\cancel{dS} - pdV - T\cancel{dS} - SdT$$

~~$dF = pdV$~~

$$dU = TdS - pdV + \mu dN$$

$$= -pdV - SdT$$

$$dG = -SdT + VdP + \mu dN$$

At a fixed temperature

$$F = -\int^{V} pdV + C(T)$$

$$= -\int \left(\frac{8t}{(3v-1)} - \frac{3}{v^2}\right)dv + C(T)$$

$$= -\frac{8t}{3}\ln(3v-1) + 3\frac{v^{-1}}{-1} + C(T)$$

$$= -\frac{8t}{3}\ln(3v-1) - \frac{3}{v} + C(T)$$

The free energy of a system minimizes, maximizes during transformation?

$\boxed{5.55}$ Van derwaals in reduced form is:

$$T = \frac{3}{8}\left(P + \frac{3}{v^2}\right)\left(v - \tfrac{1}{3}\right)$$

$$\Rightarrow \quad P(v) = \frac{\frac{8}{3}T}{v - \frac{1}{3}} - \frac{3}{v^2}$$

Then the critical values are defined when $P'(v) = P''(v) = 0$

~~thus~~ $P'(v) = \dfrac{-\frac{8}{3}T}{(v-\frac{1}{3})^2} + \dfrac{3 \cdot 2}{v^3} = 0 \qquad (1)$

$P''(v) = \dfrac{\frac{16}{3}T}{(v-\frac{1}{3})^3} - \dfrac{9 \cdot 2}{v^4} = 0 \qquad (2)$

By eq (1) $\dfrac{\frac{8}{3}T}{(v-\frac{1}{3})^2} = \dfrac{6}{v^3}$ & putting this into eq (2) gives

$$\frac{\cancel{2}}{(v-\frac{1}{3})}\,\frac{\overset{2}{\cancel{6}}}{\cancel{v}^3} - \frac{\overset{3}{\cancel{9}}\cdot\cancel{2}}{v^{\cancel{4}}} = 0 \quad \Rightarrow \quad \frac{2}{(v-\frac{1}{3})} - \frac{3}{v} = 0$$

$$\Rightarrow \quad 2v - 3\left(v - \tfrac{1}{3}\right) = 0$$

$$\Rightarrow \quad 2v - 3v + 1 = 0 \quad \Rightarrow V_{crit} = 1$$

From eq (1) $\dfrac{-\frac{\overset{2}{\cancel{8}}}{\cancel{3}}T}{\left(\frac{4}{\underset{3}{\cancel{9}}}\right)} + \dfrac{6}{1} = 0$

$$\Rightarrow \quad -\frac{2T}{\frac{1}{3}} + 6 = 0 \quad \Rightarrow \quad T_{cr} = 1$$

Then $P_{crit} = \dfrac{\frac{8}{3}}{\frac{2}{3}} - 3 = 1$

By taylors thm:

$$P(v) \cong P(1) + P'(1)(v-1) + \frac{P''(1)}{2!}(v-1)^2 + \frac{P'''(1)}{3!}(v-1)^3 + O((v-1)^4)$$

$$P(1) = \frac{\frac{8}{3}T}{\frac{2}{3}} - 3 = 4T-3$$

$$P'(v) = -\frac{\frac{8}{3}T}{(v-1/3)^2} + \frac{6}{v^3} \;;\; P'(1) = -\frac{\frac{8}{3}T}{\frac{4}{9}} + 6 = -\frac{2T}{\frac{1}{3}} + 6$$

$$= -6T+6$$

$$= -6(T-1)$$

$$P''(v) = +\frac{\frac{16}{3}T}{(v-1/3)^3} - \frac{18}{v^4} \;;\; P''(1) = \frac{\frac{16}{3}T}{(\frac{8}{27})} - 18 = \frac{2T}{\frac{1}{9}} - 18$$

$$= 18(T-1)$$

$$P'''(v) = -\frac{\frac{48}{3}T}{(v-1/3)^4} + \frac{72}{v^5} \;;\; P'''(1) = \frac{-\frac{48}{3}T}{\frac{16}{81}} + 72$$

$$= \frac{-\frac{12}{3}T}{\frac{4}{9\cdot 9}} + 4\cdot 9\cdot 2$$

$$= \frac{-T}{\frac{1}{9\cdot 9}} + 4\cdot 9\cdot 2 = -9\cdot 9\cdot T + 4\cdot 9\cdot 2 = -9(9T-8)$$

Thus

$$P(v) \cong (4T-3) - 6(T-1)(v-1) + 9(T-1)(v-1)^2 - \frac{3}{2}(9T-8)(v-1)^3 + O((v-1)^4)$$

~~Since~~ ~~$(T-1) = O(\varepsilon)$~~ Assuming uniformity in all variables towards their critical values then:

$$T - 1 = O(\varepsilon)$$

$$v - 1 = O(\varepsilon)$$

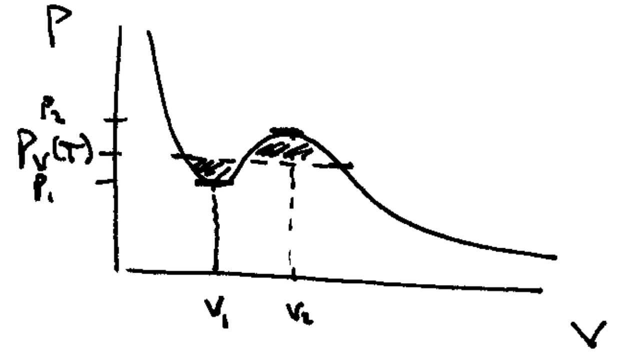
each term in the taylor expansion is of order

$$O(1) + O(\varepsilon^2) + O(\varepsilon^3) + O(\varepsilon^{3+1}) + O(\varepsilon^4)$$

Thus the $O(\varepsilon^3)$ term is the smallest. + we will drop it.

(b) Thus

$$P(v) = (4T-3) - 6(T-1)(v-1) - \frac{3}{2}(9T-8)(v-1)^3 + O((v-1)^4)$$



What are the v_1 + v_2 ?

$$P'(v) = -6(T-1) - \frac{9}{2}(9T-8)(v-1)^2 + \cancel{O(\varepsilon}v = 0.$$

$$\Rightarrow -12(T-1) - 9(9T-8)(v-1)^2 = 0$$

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$$-4(T-1) - 3(9T-8)(V-1)^2 = 0$$

$$(V-1)^2 = -\frac{4}{3}\frac{(T-1)}{(9T-8)}$$

for

$$\frac{8}{9} < T < 1$$

$$-\frac{(T-1)}{(9T-8)} > 0$$

$$\Rightarrow V = 1 \pm \sqrt{\frac{4}{3}\frac{(1-T)}{(9T-8)}}$$

Then $P_V(T)$ is given by: ? How do I do these calculations?

given $P_V(T)$

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$ By Clausius Clap. How would I get

$$(V_g - V_\ell) \propto (T_c - T)^\beta$$?

$$\Rightarrow \Delta V = \frac{L}{T\left(\frac{dP}{dT}\right)}$$

$$L = T\Delta V \frac{dP(T)}{dT}$$

⋮

(f) $\chi = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T$

$$\frac{\partial P}{\partial V}\Big|_T = -6(T-1) - \frac{9}{2}(9T-8)(V-1)^2$$

So $T \to 1^+$ $\chi \to -6(T-1)^{1}$

$T \to 1^-$ $\chi \to -6(T-1)^{1}$,

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5.56

$$\Delta S_{mixing}(x) = -R\left[x\ln x + (1-x)\ln(1-x)\right]$$

$$\frac{d\Delta S_{mixing}}{dx} = -R\left[[illegible] \ln x + \frac{x}{x} + (-1)\ln(1-x) + \frac{(1-x)(-1)}{1-x}\right]$$

$$= -R\left[\ln x - \ln(1-x)\right]$$

$$= -R\ln\left(\frac{x}{1-x}\right) = R\ln\left(\frac{x-1}{x}\right) = R\ln\left(1-\frac{1}{x}\right)$$

$$\left.\begin{array}{l} \dfrac{d\Delta S_{mixing}(0)}{dx} = R\ln(-\infty) = \text{complex } \infty \\ \dfrac{d\Delta S_{mixing}(1)}{dx} = R\ln(0) = -\infty \end{array}\right\} \text{Both } \infty$$

5.57

$$x = \frac{N_A}{N_A+N_B} \qquad 1-x = \frac{N_B}{N_A+N_B} \qquad N_A+N_B = 100$$

$$\Delta S_{mixing}(x) = -R\left[x\ln x + (1-x)\ln(1-x)\right]$$

$$x = \frac{N_A}{100} \qquad N_A = 0 \qquad \Delta S_{mixing}(0) = 0$$

$$\Delta S_{mixing}(1) = -R\left[\frac{1}{100}\ln\left(\frac{1}{100}\right) + \left(\frac{99}{100}\right)\ln\left(\frac{99}{100}\right)\right]$$

$nR = Nk$

$$R = \left(\frac{N}{n}\right)k$$

$$\Delta S_{increase} = \Delta S_{mixing}(1) - \Delta S_{mix}(0) =$$

$$\Delta S_{mixing}(2) = -R\left[\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\right]$$

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5.8B

(a) $U_0 \cdot n \cdot \frac{N}{2}$

(b) let $x = \frac{N_B}{N}$. When mixed a given atom will have $x \cdot n$ of its neighboring molecules of type B & $(1-x)n$ of its neighbors of type A. (on average)

Then a molecule of type A will have potential energy of

$$\frac{1}{2}\Big[\underbrace{(x \cdot n U_0 + (1-x)\, n U_{AB})}_{\text{potential energy of each B centered bond}} \underset{\uparrow}{xN} + \underbrace{(x n U_{AB} + (1-x) n U_0)}_{\text{potential energy of each A centered bond}} \underset{\uparrow}{(1-x)N}\Big] = U_{total}$$

$\uparrow$ Avoid double counting. ($\frac{1}{2}$)

$\uparrow$ # of B centered Bonds (xN)

$\uparrow$ # of each A centered bonds ($(1-x)N$)

$$\rightarrow U_{total} = \frac{1}{2}N\left[x^2 n U_0 + x(1-x) n U_{AB} + x(1-x) n U_{AB} + (1-x)^2 n U_0\right]$$

$$= \frac{1}{2}Nn\left[(x^2 + (1-x)^2)U_0 + 2x(1-x)U_{AB}\right]$$

$$= \frac{1}{2}Nn\left[(2x^2 - 2x + 1)U_0 + 2x(1-x)U_{AB}\right]$$

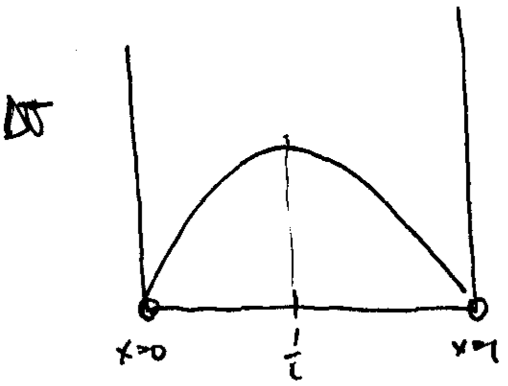
(c) $\Delta U_{\text{potential}} = U_{\text{mixed}} - U_{\text{unmixed}}$

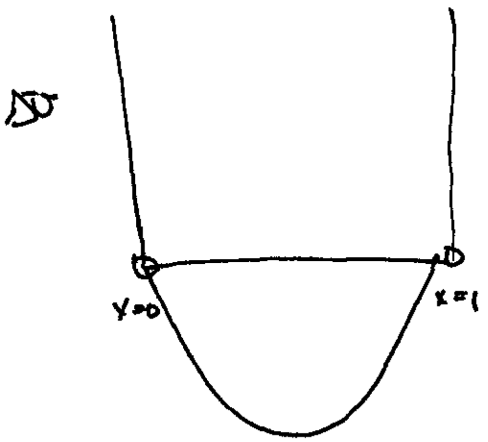
$= \frac{1}{2}Nn\left[2x(x-1)U_0 + 2x(1-x)U_{AB}\right]$ $0 \le x \le 1$

$= \frac{1}{2}Nn\, x(1-x)\left[U_{AB} - U_0\right]$ $1-2x=0.$

Assum $U_{AB} - U_0 > 0$

$U_{AB} - U_0 < 0$





(d) $\frac{d\Delta U_{pot}}{dx} = C(1-x) - Cx = C(1-2x) \neq \infty.$

$nR = Nk$

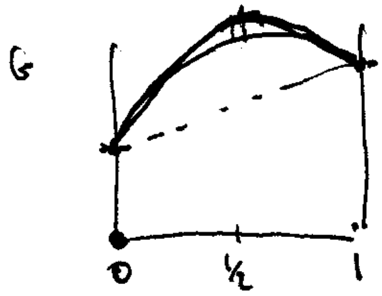
$N = \frac{nR}{k}$

(e) $G = (1-x)G_A^\circ + xG_B^\circ + RT\left[x\ln x + (1-x)\ln(1-x)\right]$

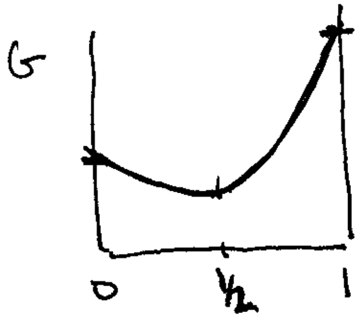
$+ \frac{1}{2}Nn\,x(1-x)(U_{AB} - U_0)$

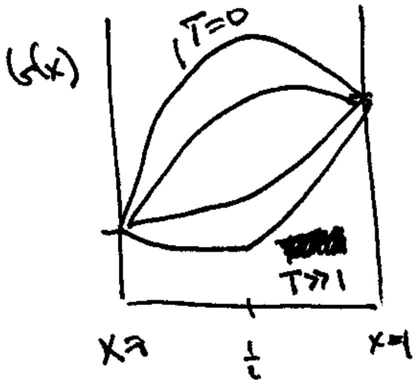
$\Rightarrow G = (1-x)G_A^\circ + xG_B^\circ + \frac{1}{2}Nn\,x(1-x)(U_{AB} - U_0) + RT\left[x\ln x + (1-x)\ln(1-x)\right]$

T≪1



T≫1



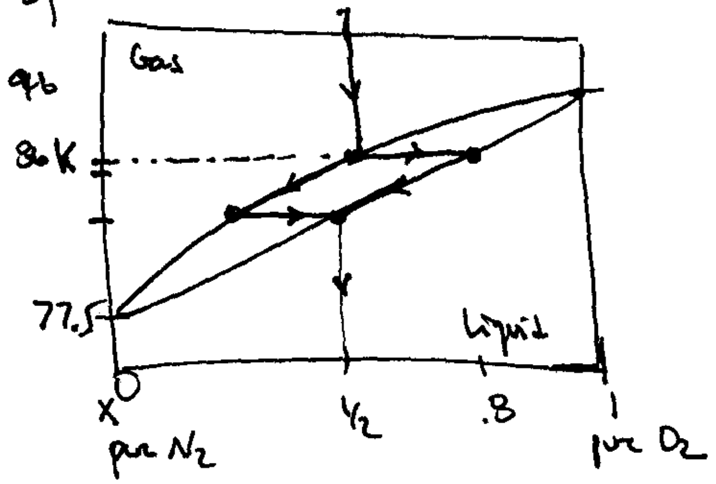


(f) How get Solubility gap?

(g) ?

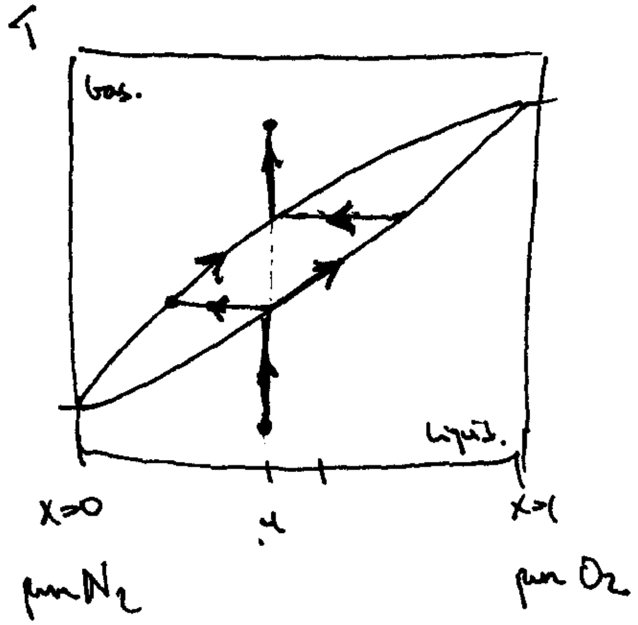
(h) ?

5.59 From Fig 5.31



From the diagram, the gas cools as a mixture until about 86K. A horizontal line intersects the liquid line at about x=.8, so the liquid that forms is 80% O_2. As the temperature is cooled further, the fractional amount of O_2 in the gas + the liquid decrease. ~~[illegible]~~ until about 82K, at which point the gibbs free energy of the entire liquid phase is lower than the gas phase + one has entire liquid.

5.60



12-04-02

As the liquid heats up, at around 80.5K a liquid + gas phase forms, initially the gas is of concentration $x \cong .2$ or 20% O_2 + 80% N_2, The concentration of O_2 increases in both the gas + the liquid until about T = 84K when the mixture becomes entirely gas.

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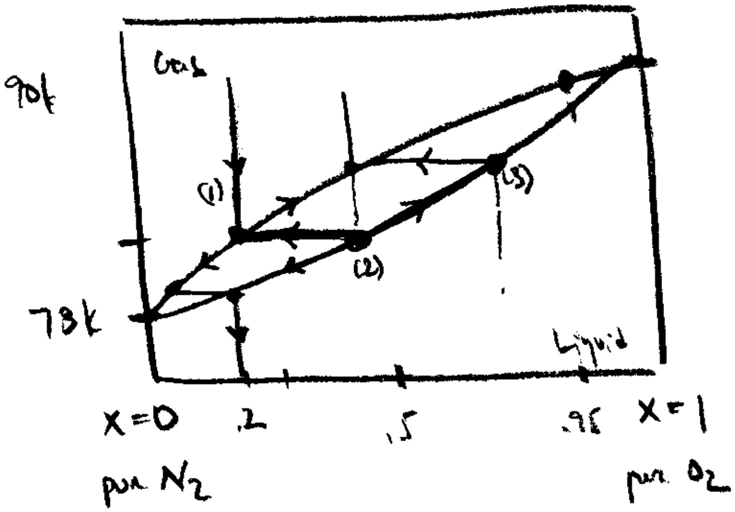
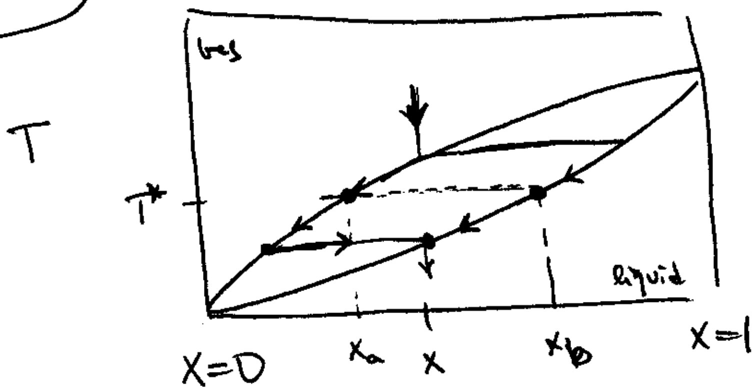
(5.61) O_2 95% pure

Assume air is 79% N_2 + 21% O_2



Given initial gas (air) cool it until liquid 1st begins to form. This liquid is ≈ .5 % O_2! Then holding the temperature constant, pump off the gas above the liquid. Then let the temperature increase again, the liquid will then increase in % of O_2 w/ each cycle in this manner.

(Prob 5.62)



It

$$\frac{\text{Amt liquid}}{\text{Amt Gas}} = \frac{x - x_a}{x_b - x}$$

$$\Rightarrow (\text{Amt of liquid})(x_b - x) = (\text{Amt} \overset{\text{of}}{\wedge} \text{Gas})(x - x_a)$$

$$\Rightarrow A_L x_b - A_L x = A_G x - A_G x_a$$

$$(A_G + A_L)\,x = A_L x_b + A_G x_a$$

$$\Rightarrow x = \frac{A_L}{A_G + A_L} x_b + \frac{A_G}{A_G + A_L} x_a$$

$$\Rightarrow x = \frac{A_G}{A_G + A_L} x_a + \frac{A_L}{A_L + A_G} x_b \quad \ldots \quad ?$$

(5.63)

$$= \quad G = U + PV - TS$$

$$dG = dU + V\,dP - S\,dT \Rightarrow \frac{\partial G}{\partial P} = V > 0$$

∴ ~~Both~~ As $P \nearrow$ Both phases Gibbs free energy would increase.

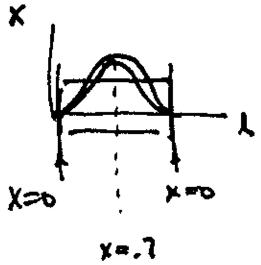
12-09-02

since the volume phase has $V_{gas} > V_{liquid}$

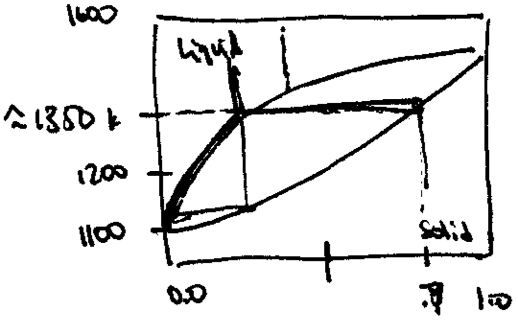
$\frac{\partial G_{gas}}{\partial P} > \frac{\partial G_{liquid}}{\partial P}$ + the gases' gibbs free energy

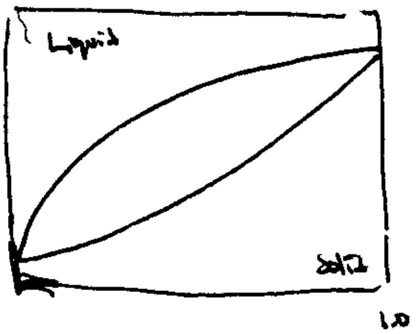
I would expect the change in pressure to make the sliver in the T-x diagram smaller.

5.64



(a) ?

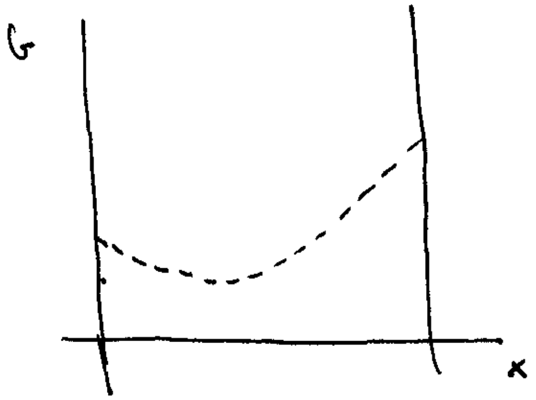


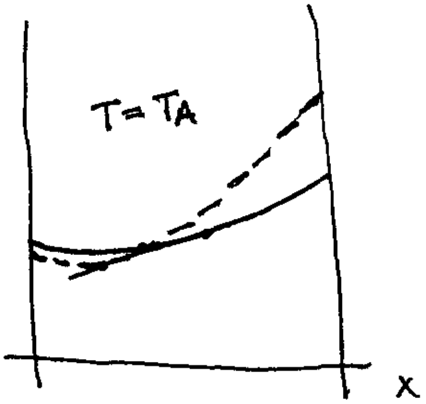


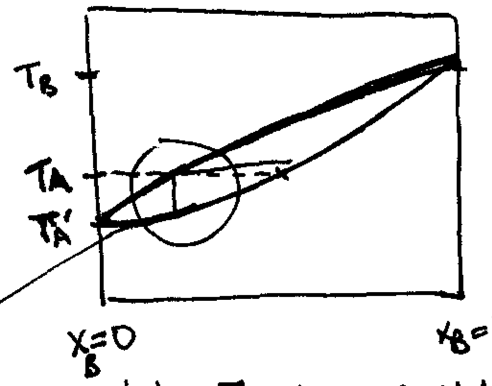
(b) ?

5.65 Free energy of liquid (substantial positive energy) & graph is much flatter

Similar structure as in Fig 5.30 but w/ final temp corresponding different than shown



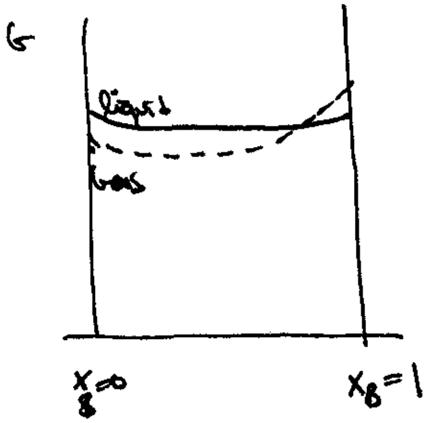


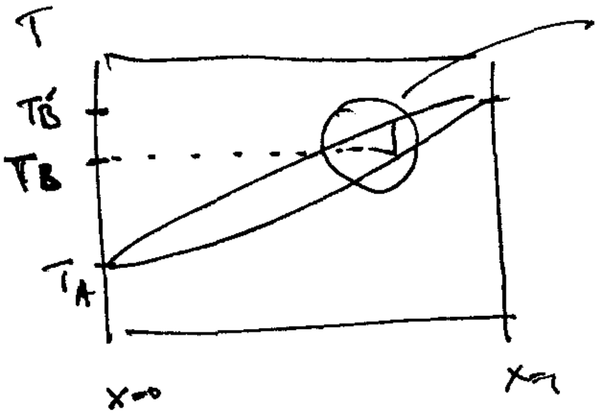


Not sure what happens?

something happens here since below T_A the pure substance A

5.66





Not sure how the cut off goes...

(8.67) $\mu \equiv \frac{\partial G}{\partial N}$

Since $G = (1-x)G_A^0 + xG_B^0 + RT\left[x\ln x + (1-x)\ln(1-x)\right]$

(a)

$$\frac{\partial}{\partial N_A} = $$

$$= \frac{\partial x}{\partial N_A}\frac{\partial}{\partial x}.$$

$$x = \frac{N_B}{N_A+N_B}$$

$$\frac{\partial x}{\partial N_A} = \frac{-N_B}{(N_A+N_B)^2} = \frac{-x}{N}.$$

$$\frac{\partial x}{\partial N_B} = \frac{1}{(N_A+N_B)} - \frac{N_B}{(N_A+N_B)^2}$$

$$= \frac{N_A+N_B-N_B}{(N_A+N_B)^2} = \frac{N_A}{(N_A+N_B)^2}$$

$$= \frac{(1-x)}{N}$$

∴

$$\mu_A = \frac{\partial G}{\partial N_A} = \frac{-x}{N}\frac{\partial G}{\partial x}$$

$$= \frac{-x}{N}\Big[-G_A^0 + G_B^0$$

$$+ RT\left[\ln x + \cancel{1} - \ln(1-x) - \cancel{1}\right]$$

$$nR = Nk$$

$$\frac{R}{N} = \frac{k}{n}$$

$$= \frac{-x}{N}\left[-G_A^0 + G_B^0 + RT\left(\ln x - \ln(1-x)\right)\right] \; ?$$

Assume $\mu_A = \mu_A^0 + kT\ln(1-x)$

& $\mu_B = \mu_B^0 + kT\ln x$

(b) $\mu_A(T) = \mu_B(T)$

$$\Rightarrow \mu_A^0 + kT\ln(1-x) = \mu_B^0 + kT\ln x$$

$$\frac{\mu_A^0 - \mu_B^0}{kT} = \ln x - \ln(1-x) = \ln\left(\frac{x}{1-x}\right)$$

12-08-02

Assume $\mu_B = \mu_B^0 + kT\ln(1-x)$

Then equality of chemical potential ⇒

$$\mu_A = \mu_B$$

$$\mu_l^0 + kT\ln(1-x_l) = \mu_g^0 + kT\ln(1-x_g)$$

$\{nR = kN\}$

$$\underbrace{\frac{\mu_l^0 - \mu_g^0}{kT}} = \ln\left(\frac{1-x_l}{1-x_g}\right)$$

Assuming $\mu_l^0 \equiv \frac{G_l^0}{N_A}$

$\mu_g^0 = \frac{G_g^0}{N_A}$ we get

$$\exp\left\{\frac{\Delta G_{lg}}{RT}\right\} \overset{?}{=} \frac{1-x_l}{1-x_g}$$

$$(1-x_g)\,e^{\frac{\Delta G}{RT}} = (1-x_l)$$

& $e^{\frac{\Delta G}{RT}} - 1 =$

(c) Assuming: $\Delta G^0_{\{A,B\}} = \Delta H^0 - T\Delta S^0$. gives:

$$\frac{1-x_l}{1-x_g} = \exp\left\{\frac{\Delta H_A^0 - T_A\Delta S_A}{RT}\right\}$$

$$\frac{x_l}{x_g} = \exp\left\{\frac{\Delta H_B^0 - T\Delta S_B}{RT}\right\}$$

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(5.68) $w_{\ell} = .67$ plumbers ~~[illegible]~~ solder.

$w_{tin} = .33$

As it cools 1st $\underset{\overset{\shortparallel}{Pb}}{\beta}$ solidify's then tin, the solid Pb might ~~[illegible]~~ to the ~~bottom~~ allowing the tin to solidify on top of it, ~~[illegible]~~ preventing its contact w/ H_2O.

(5.69) Some salt gets into the ~~[illegible]~~ ice lowering its freezing point, so that ~~for~~ the given composition the H_2O salt mixture would stay a liquid rather than a solid.

If the temp is super low, then one ~~[illegible]~~ ~~[illegible]~~ would/could end up w/ a mixture that is required to be a solid still.

(5.70) When you add salt to the ice bath you lower the ~~[illegible]~~ freezing temperature of the ~~[illegible]~~ ice — H_2O mixture. ~~[illegible]~~ ~~[illegible]~~ ~~allows~~ the ~~ice salt mixture to [illegible] absorb more~~

Somehow by lowering the freezing temperature we are able to extract heat from the ~~ice~~ ~~cream~~, ~~causing~~ ~~it to~~ ~~the~~ milk sugar mixture of ice cream, causing it to freeze.

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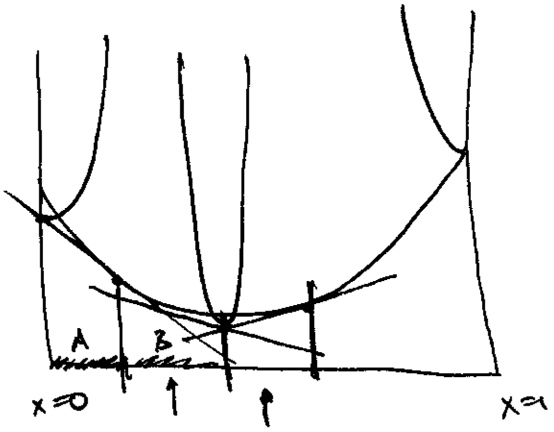
(5.71)



$$\frac{\partial G}{\partial T} = -S$$

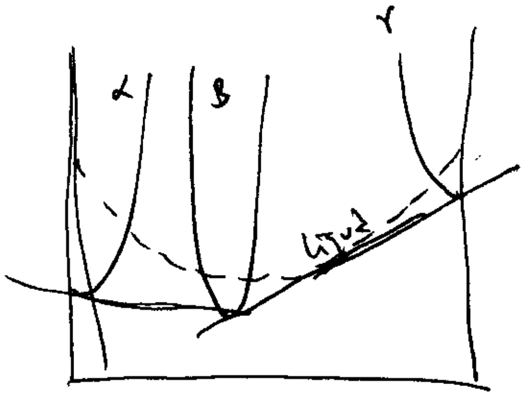
$$S_{liquid} > S_{solid}$$

$$\frac{\partial G_{liquid}}{\partial T} < \frac{\partial G_{solid}}{\partial T}$$

$$\left\{ -S_{liq} < -S_{solid} \right\}$$

$$S_{liq} > S_{solid}$$ ✓

(5.72)



$$\Omega \propto N_A$$

$$S \propto k \ln \Omega$$

$$dS = k \ln N_A$$

$$\cancel{dG} = f(T,P)$$

$$dG = \underbrace{dU + PdV} - Tk \ln N_A - T\underbrace{dS}_{\text{ind of } N_A}$$

$$= f(T,P) - Tk \ln N_A$$

÷ by # duplicated states
= 2

$$dG = 2f(T,P) - 2kT \ln N_A + kT \ln 2$$

$$dG = N_B f(T,P) - N_B kT \ln N_A + kT \ln N_B!$$

$$\uparrow$$

$$= N_B f(T,P) - N_B kT \ln N_A$$

$$N_B \ln N_B - N_B$$

$$G = N_A \mu_0(T,P) + N_B f(T,P) - N_B kT \ln N_A + N_B kT \ln N_B - N_B kT \quad \text{eq } 5.68$$

$$\mu_A = \left.\frac{\partial G}{\partial N_A}\right|_{T,P,N_B} = \mu_0(T,P) - \frac{N_B kT}{N_A}$$

$$\mu_B = \left.\frac{\partial G}{\partial N_B}\right|_{\dots} = f(T,P) - kT \ln N_A + kT \{ \ln N_B \}$$

$$= f(T,P) + kT \ln\left(\frac{N_B}{N_A}\right)$$

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molality = $\dfrac{\text{moles solute}}{\text{kilograms of solvent}}$ "$\dfrac{\text{mol}}{\text{kg}}$"

$$N_B = N_{Avg} \cdot n_B$$

$$N_A = N_{Avg} \cdot n_A$$

$$\text{kilogram solvent} = M \cdot n_A = M \cdot \frac{N_A}{N_{Avg}}$$

$$m = \frac{n_B}{M \cdot n_A} = \frac{N_B/\cancel{N_{Avg}}}{M\, N_A/\cancel{N_{Avg}}} = \left(\frac{1}{M}\right)\frac{N_B}{N_A}$$

$\therefore$

$$\mu_B = f(T,P) + kT \ln(M \cdot m)$$

$$= \mu^0(T,P) + kT \ln(m_B)$$

(5.73) let $N_A = rN_A$

$N_B = rN_B$

$$G' = rN_A\mu_0(T,P) + rN_Bf(T,P) - rN_BkT\ln(rN_A) + rN_BkT\ln(rN_B) - rN_BkT$$

$$= rN_A\mu_0(T,P) + rN_Bf(T,P) - rN_BkT\ln(N_A) - rN_B\cancel{kT}\ln(r) + rN_BkT\ln(N_B) + rN_B\cancel{kT}\ln(r) - rN_BkT$$

$$= r\{\underbrace{N_A\mu_0(T,P) + N_Bf(T,P) - N_BkT\ln(N_A) + N_BkT\ln(N_B)}_{G} - N_BkT]$$

$= rG.$

w/o $N_BkT\ln(N_B) - N_BkT$ or $kT\ln(N_B!)$ term we wouldn't have the condition shown.

(5.74) 5.69 5.70 $G = N_A\mu_A + N_B\mu_B$

Now $N_A\mu_A + N_B\mu_B = N_A\mu_0(T,P) - N_BkT + N_Bf(T,P) + kTN_B\ln(N_B/N_A)$

$= N_A\mu_0(T,P) - N_BkT + N_Bf(T,P) + kTN_B\ln(N_B) - kTN_B\ln(N_A)$

Yes

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5.75

5.68 dilute solution

$$G = N_A \mu_0(T,P) + N_B f(T,P)$$
$$- N_B kT \ln(N_A) + N_B kT \ln N_B$$
$$- N_B kT$$

5.61 ideal mixture

$$G = (1-x) G_A^\circ + x G_B^\circ$$
$$+ RT\left[x \ln x + (1-x)\ln(1-x)\right]$$

$G_A^\circ = N_A \mu_A^\circ(T,P)$ $x = \frac{N_B}{N_A+N_B}$; $1-x = \frac{N_A}{N_A+N_B}$

$G_B^\circ = N_B \mu_B^\circ(T,P)$ if $N_B \ll N_A$

$x \simeq \frac{N_B}{N_A}$ + $1-x \cong 1$

Then $G = N_A \mu_A^\circ(T,P) + \frac{N_B}{N_A} \cdot N_B \mu_B^\circ(T,P)$

$\overset{?}{n} RT = NkT$

$$+ RT\left[\frac{N_B}{N_A} \ln\left(\frac{N_B}{N_A}\right) + (\quad \cdot\cdot \quad \right]$$

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$$\mu_A = \mu_0(T,P) - \frac{N_B kT}{N_A}$$ 5.69

A ~~solute~~ solvent, B ~~solvent~~ solute

$$\mu_B = f(T,P) + kT\ln\left(\frac{N_B}{N_A}\right)$$ 5.70

$$\mu_0(T,P_2) = \mu_0(T,P_1) - \frac{N_B kT}{N_A}$$

$P_2 > P_1$

$$\mu_0(T,P_2) \approx \mu_0(T,P_1) + (P_2-P_1)\frac{\partial \mu_0}{\partial P}$$

$$(P_2-P_1)\frac{\partial \mu_0}{\partial P} = -\frac{N_B}{N_A}kT$$

$$\frac{\partial \mu_0}{\partial P} = \frac{\partial (G/N)}{\partial P} = \frac{1}{N}\frac{\partial G}{\partial P}$$

$$= \frac{V}{N}$$

$$(P_2-P_1)\frac{V}{\cancel{N_A}} = \frac{N_B kT}{\cancel{N_A}}$$

$$P_2 - P_1 = \frac{N_B kT}{V} = \frac{n_B RT}{V}$$

$$dG = dU + PdV - TdS$$

~~$dG = dU + PdV - SdT$~~

But $dU = TdS - PdV + \mu dN$

$\therefore$

~~$dG = TdS - PdV$~~

$$G = U + PV - ST$$

$$H = U + PV$$

$$dG = \underset{\sim}{dU} + \cancel{PdV} + VdP - SdT - \cancel{TdS}$$

$$= \cancel{TdS} - \cancel{PdV} + \mu dN$$

$$= VdP - SdT + \mu dN$$

$$\left.\frac{\partial G}{\partial P}\right|_{T,N} = V$$

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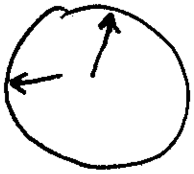
$$\frac{n_B}{V} = \left(\frac{1}{200}\right)\left(\frac{1\,\text{mole}}{18\,\text{cm}^3}\right)\left(\frac{100\,\text{cm}}{1\,\text{m}}\right)^3 = \ . \ —$$



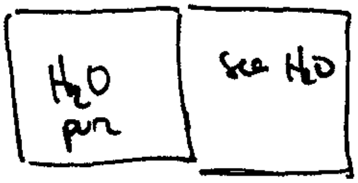
$$P_2 - P_1 = \frac{n_B RT}{V}$$

$$= (278\ \text{mol}/\text{m}^3)(8.314\ \text{J}/\text{mol}\cdot\text{k})(300\text{k}) \cong 7 \cdot 10^5\ \text{N}/\text{m}^2$$

$10^5 \cong 1$ Atm

(5.86) 1kg sea H_2O

(a)



$$P_2 - P_1 = \frac{n_B RT}{V}$$

$$35\text{g NaCl} = \frac{35\text{ g}}{(23+35)\text{ g/mol}} = \left(\frac{35}{58}\right)\text{mol}$$

$V = 1\text{kg }(H_2O)$ $1\text{g} = 1\text{cm}^3$

$$= 1000\text{ g}\,\frac{1\text{cm}^3}{1\text{g}}\cdot\left(\frac{1\text{m}}{100\text{cm}}\right)^3 = \frac{10^3}{10^6} = 10^{-3}\text{ m}^3$$

So $\frac{n_B}{V} = \left(\frac{35/58}{10^{-3}}\right)\frac{\text{mol}}{\text{m}^3}$

(b)

1 liter sea H_2O. $= \square\,\text{m}^3$

$\Leftarrow P > P_2 = P_1 + \frac{n_B}{V}\cdot RT$

Assuming a side of 1m^2

$W \geq [P(1\text{m}^2)]\cdot\Delta l$

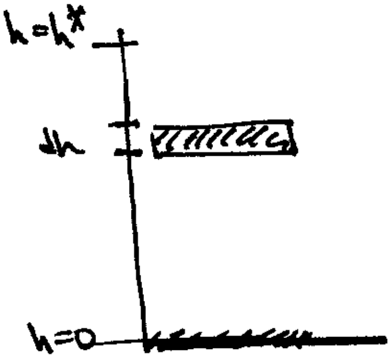
(5.77) $(\text{grms}/\text{liter}) \cdot M^{-1}$ moles/l

$C\,(\text{grams}/l)$

M = molecular weight

g/mol.

$$P_2 - P_1 = \cancel{\int_{h=0}^{h^*} dh \cdot A\, \rho g h}$$



$= \cancel{A}\rho g$ $F = m\cdot g$; $P = \frac{F}{A}$

$= V\cdot\rho\cdot g$

$F = \Delta h\cdot\rho\cdot A\cdot g$ $\therefore$ $P_2 - P_1 = \Delta h\cdot g\cdot\rho = \frac{n_B RT}{V}$

plotting [H] v.s. Δh * $\frac{\Delta h\cdot g\cdot\rho}{RT} = \frac{n_B}{V}$ = moles/liter

*

$\frac{[H]}{M}$ = moles/liter

$$\therefore \frac{\overset{\checkmark}{\Delta h}\cdot g\cdot\rho}{RT} = \frac{\overset{\checkmark}{[H]}}{M}$$

(5.78) ?

$$-(T-T_0)\underbrace{\left[\left(\frac{S}{N}\right)_{liq} - \left(\frac{S}{N}\right)_{gas}\right]}_{\frac{-L}{N_A T_0}} = \frac{N_B kT}{N_A}$$

let $N = N_A$

or $$T - T_0 = \frac{N_B k T T_0}{L} \cong \frac{N_B k T_0^2}{L}$$ eq 5.90

$$NaCl = 23 + 35 = 58 \text{ g/mol}$$

$$\text{Avg Atomic mass} = \frac{1}{2}(23+35) = \frac{58}{2} \cong 25 + 1.5 \doteq 26.5$$

$$T - T_0 = \frac{(1.2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(373\,\text{K})^2}{2260\,\text{kJ}} \qquad N_B k = n_B R$$

$$= .6\,\text{K}$$

$$P - P_0 = -\frac{N_B}{N_A}P_0 = -\frac{n_B}{n_A}P_0 = -\frac{1.2}{\left(\frac{1000}{18}\right)}P_0$$

B is solvent

A is solute.

Prob 5.79

1 teaspoon = 1kJ amt of salt

$\cong$ 10 grams NaCl

$= \frac{40}{[illegible]} = \frac{10}{23+35}$ moles $= \frac{10}{\ } \equiv n_B$

$T - T_0 = \frac{n_B (R)(373\,K)^2}{2260\,kJ} < .6\,k$. has negligible effect

Prob 5.80 eq 5.90 $T - T_0 = \frac{n_B R T_0^2}{L}$

Clausius-Clapeyron: $\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\Delta S}{\Delta V}$

w/ $\frac{P}{P_0} = 1 - \frac{n_B}{n_A}$ Raoult's law

$\frac{dP}{dT} = \frac{L}{T\Delta V} \Rightarrow dT = \left(\frac{T\Delta V}{L}\right) dP$

Assuming $\frac{T\Delta V}{L}$ is a constant as our transformation takes place from $T_0 \to T$, $P_0 \to P$

one gets $T - T_0 = \frac{T_0 \Delta V_0}{L}(P - P_0) = \frac{T_0 \Delta V_0}{L}\left(-\frac{n_B P_0}{n_A}\right)$ By Raoult's law

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But $\{PV = nRT\}$ + Assuming

$$T - T_0 = -\frac{T_0}{L\,n_A}(P\Delta V)\,n_B$$

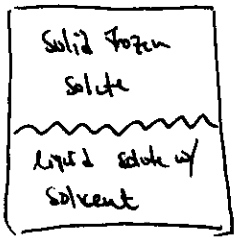
A is solvent

$$= -\frac{T_0}{L\cancel{n_A}}\,n_B(\cancel{n_A}RT_0) = \text{[illegible]}$$

$$= -n_B\frac{RT_0^2}{L}$$

off by a minus sign? why?

Prob 5.81



$\{T - T_0 < 0\}$

By eq

$$\mu_{A,solid}(P,T) = \mu_{A,liq}(P,T)$$
$$\parallel$$
$$\mu_0(T,P) - \frac{N_B}{N_A}kT \qquad \text{(By eq 5.69)}$$

Holding the pressure fixed to investigate changes in temperature only we get

$$\mu_{A,solid}(P,T) = \mu_{A,solid}(P,T_0) + (T-T_0)\frac{\partial\mu_{A,solid}}{\partial T}(P,T_0)$$

$$\underbrace{\mu_0(P,T)} \triangleq \mu_0(P,T_0) + (T-T_0)\frac{\partial\mu_0}{\partial T}(P,T_0)$$

chem potential of ~~solution~~ of solvent only in liquid phase

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Then we get

$$\mu_{A,\text{solid}}(\cancel{P},T_0) + (T-T_0)\frac{\partial \mu_{A,\text{solid}}}{\partial T} = \mu_0(\cancel{P},T_0) + (T-T_0)\frac{\partial \mu_0}{\partial T}(P,T) - \frac{N_B}{N_A}kT$$

$$d\left\{ \frac{\partial \mu}{\partial T} = \frac{\partial}{\partial T}\left(\frac{G}{N}\right) = \frac{1}{N}\frac{\partial G}{\partial T} = -\frac{S}{N} \right\}$$

$$G = U + PV - TS$$

$$dU = TdS - pdV$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$= T\cancel{dS} - p\cancel{dV} + \cancel{pdV} + VdP - \cancel{T}dS - SdT$$

$$= VdP - SdT$$

$$\therefore \quad \frac{(T-T_0)}{N_A}\Big[\underbrace{S_{A,\text{solid}} - S_{A,\text{liquid}}}_{(-L/T)}\Big] = -\frac{N_B}{N_A}kT$$

$$T - T_0 = \frac{N_B k T^2}{L}$$ ... what went wrong?

(Prob 5.82) One would get the exact same result as for the boiling point elevation as in the text?