Problem Set 2
Solutions
3.20 MIT
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Problem 1.1

$$S(U, V) : dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Variables here are U and V and intensive variables are $\frac{1}{T}$ and $\frac{P}{T}$.

To go to $\frac{1}{T}$ as a natural variables take the Legendre transform by subtracting $\frac{U}{T}$ from S

$$J = S - \frac{U}{T}$$

So,

$$dJ = -Ud\left(\frac{1}{T}\right) + \frac{P}{T}dV$$

Note that J is equal to $-\frac{F}{T}$ (F is the Helmholtz energy)
Similarly, go from $S(U, V)$ to $B(U, \frac{P}{T})$ by taking

$$B = S - \frac{P}{T}V$$

$$dB = \frac{1}{T}dU - Vd\left(\frac{P}{T}\right)$$

A Legendre transform with respect to both U and V defines the Planck function (Yes, you too can be famous by defining your own Legendre transform)

$$Y = S - \frac{P}{T}V - \frac{U}{T}$$

$$dY = -Ud\left(\frac{1}{T}\right) - Vd\left(\frac{P}{T}\right)$$

One can show that these functions have extrema properties just like the Legendre transforms of energy. Massieu functions are maximum under constant value of their natural variables.

Problem 1.2

We know that C_p is defined as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P$$

Enthalpy can be obtained from the Legendre transform of the internal energy as follows,

$$H = U + PV$$

We know that for an ideal gas U is a function of temperature only and the $PV = RT$ (for one mole), thus

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + \frac{\partial}{\partial T}(RT)$$

$\left(\frac{\partial U}{\partial T} \right)_P$ is only a function of temperature and this is not a function of pressure. Also, R is not a function of pressure. So C_p of an ideal gas must be independent of pressure.

Problem 1.3

$$F = F(T, V)$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

Compare this with

$$F = U - TS$$

$$dF = -SdT - PdV$$

Therefore,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

Using the given formula for F, solve for P by taking the derivative w.r.t V at constant T.

$$\left(\frac{\partial F}{\partial V}\right)_T = \frac{a}{V_m^2} - \frac{RT}{V_m - b} + \left(\frac{\partial f}{\partial V}\right)_T$$

Since f(T) is only a function of T, this term drops out and the solution is:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Problem 1.4

(a) We can write the differential form of the entropy as a function of T and P

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying by T to get TdS (which is equal to dQ)

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

Since we are told the process is adiabatic, $TdS = \partial q = 0$, so,

$$-T\left(\frac{\partial S}{\partial P}\right)_T dP = T\left(\frac{\partial S}{\partial T}\right)_P dT$$

Or,

$$\left(\frac{dT}{dP}\right) = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\frac{C_p}{T}} = \frac{T\alpha V}{C_p}$$

(b) Using the above relationship, we can get a value for the final temperature,

$$\int \frac{dT}{T} = \int \frac{\alpha V}{C_p} dP$$

$$\ln\left(\frac{T_f}{T_i}\right) = \frac{\alpha V}{C_p}\Delta P$$

$$T_f = T_i \exp\left[\frac{\alpha V}{C_p}\Delta P\right]$$

For this case we can assume we have 1kg of material which means the volumes is 0.001 m³.
Remember that $\alpha_V = 3\alpha_L$

$$T_f = 300 * \exp\left[\frac{3 \cdot 19 \times 10^{-5}K^{-1} * 0.001m^3 * 999atm * 1.01 \times 10^5 Pa/atm}{2.3J/g \cdot K * 1000g}\right]$$

$$T_f = 300 * 1.0254 = 307.6K$$

The only trick here is to be careful with your units and the definition of α_L and α_V.

Problem 1.5

(a) Start with the internal energy

$$dU = TdS - PdV + HdM$$

Using a Legendre transformation get $G(T, P, H)$

$$G = U - ST + PV - HM$$

$$dG = -SdT + VdP - MdH$$

And since we know that the order of differentiation does not matter

$$\left(\frac{\partial^2 G}{\partial H \partial P}\right) = \left(\frac{\partial^2 G}{\partial P \partial H}\right)$$

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

$$\left(\frac{\partial V}{\partial H}\right)_{P,T} = -\left(\frac{\partial M}{\partial P}\right)_{H,T}$$

(b) One possibility is

$$\left(\frac{\partial S}{\partial H}\right)_{T,P} = \left(\frac{\partial M}{\partial T}\right)_{H,P}$$

Problem 1.6

(a)

$$U = TdS + \tau dL$$

$$G = U - TS$$

$$dG = SdT + \tau dL - TdS + SdT$$

Which yields the solution:

$$dG = \tau dL - SdT$$

(b)We also know if G=G(L,T) that

$$dG = \left(\frac{\partial G}{\partial L}\right)_T dL + \left(\frac{\partial G}{\partial T}\right)_L dT$$

Thus,

$$\tau = \left(\frac{\partial G}{\partial L}\right)_T \text{ and } S = -\left(\frac{\partial G}{\partial T}\right)_L$$

Since we know that dG is a perfect differential, then the second derivatives must be equal independent of the order which they are taken.
So,

$$\left(\frac{\partial^2 G}{\partial T \partial L}\right) = \left(\frac{\partial^2 G}{\partial L \partial T}\right)$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial L}\right)_T\right)_L = \left(\frac{\partial}{\partial L}\left(\frac{\partial G}{\partial T}\right)_L\right)_T$$

$$\left(\frac{\partial \tau}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T$$

(c)

$$dU = TdS + \tau dL$$

$$\left(\frac{\partial U}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + \tau$$

Using the relation from part (b),

$$\left(\frac{\partial U}{\partial L}\right)_T = -T\left(\frac{\partial \tau}{\partial T}\right)_L + \tau$$

(d) If U is only a function of temperature, then

$$\left(\frac{\partial U}{\partial L}\right)T = 0 = \tau - T\left(\frac{\partial \tau}{\partial T}\right)_L$$

$$\frac{1}{\tau}\left(\frac{\partial \tau}{\partial T}\right)_L = \frac{1}{T}$$

LEVEL 2 PROBLEMS

Problem 2.1

(a) Start by constructing the differential form of S(T,P) [In Zemansky this is called the second TdS equation]

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

But we know $T\left(\frac{\partial S}{\partial T}\right)_P = C_p$ and from a Maxwell relation we know $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ .So,

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_p dT - TV\alpha dP$$

For an isothermal compression,

$$Q = TdS = -T\int V\alpha dP$$

In the case of a solid or liquid, neither V or α is very sensitive to pressure. So,

$$Q = -TV\alpha \int dP = -TV\alpha\Delta P$$

Now we can use the data given to calculate Q (Replacing V with M/ρ)

$$Q = \frac{-TM\alpha\Delta P}{\rho} = -\frac{298K * 0.5kg * 49.5 \times 10^{-6}K^{-1} * 5.05 \times 10^8 Pa}{8.96 \times 10^3 kg/m^3}$$

$$Q = -416J$$

(b)We now need to calculate the work during the compression

$$W = -\int PdV$$

$$W = -\int \left(\frac{\partial V}{\partial P}\right)_T PdP$$

$$W = \int V\beta PdP = V\beta \int PdP = \frac{V\beta}{2}\left(P_f^2 - P_i^2\right)$$

$$W = \frac{M\beta}{2\rho}\left(P_f^2\right) = \frac{0.5kg * 6.18 \times 10^{-12}Pa^{-1}}{2 * 8.96 \times 10^3 kg/m^3} * \left(5.05 \times 10^8 Pa\right)^2$$

$$W = 44J$$

(c) We know the first law,

$$\Delta U = Q + W = -416J + 44J$$

$$\Delta U = -372J$$

Thus it can be seen that the extra amount of energy in the form of heat comes from the storage of internal energy.

(d) Now we can go back to the relationship we obtained for TdS (which we know is 0 since the process is adiabatic and reversible)

$$TdS = 0 = C_p dT - TV\alpha dP$$

$$\int \frac{dT}{T} = \int \frac{\alpha V}{C_p}dP$$

$$\ln\left(\frac{T_f}{T_i}\right) = \frac{\alpha V}{C_p}\Delta P$$

$$T_f = T_i \exp\left[\frac{\alpha V}{C_p}\Delta P\right] = T_i \exp\left[\frac{\alpha M}{C_p \rho}\Delta P\right]$$

$$T_f = 298 \exp\left[\frac{0.5kg * 49.5 \times 10^{-6}K^{-1} * 5000atm * 1.01 \times 10^5 Pa/atm}{8.96 \times 10^3 kg/m^3 * 385J/kg \cdot K * 0.5kg}\right]$$

$$T_f = 300K$$

$$\Delta T = 300 - 298 = 2K$$

Problem 2.2

In terms of T and P, dU can be written

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

We can evaluate the two partials $\left(\frac{\partial U}{\partial T}\right)_P$ and $\left(\frac{\partial U}{\partial P}\right)_T$ using $U(S,V)$ which we know

$$dU = TdS - PdV$$

So

$$\left(\frac{\partial U}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P$$

Which can be simplified since we know $C_p = T \left(\frac{\partial S}{\partial T}\right)_P$ and $V\alpha = \left(\frac{\partial V}{\partial T}\right)_P$

$$\left(\frac{\partial U}{\partial T}\right)_P = C_p - PV\alpha$$

Similarly

$$\left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T$$

which can be simplified using the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$ and $V\beta = - \left(\frac{\partial V}{\partial P}\right)_T$

$$\left(\frac{\partial U}{\partial P}\right)_T = -TV\alpha + PV\beta = V(\beta P - \alpha T)$$

Putting this all together,

$$dU = (C_P - PV\alpha)\,dT + V(\beta P - \alpha T)\,dP$$

Problem 2.3

Given the definition of dH : $dH \equiv TdS + VdP$, we want first to determine how the enthalpy varies with pressure, at *constant* temperature:

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

By using the Maxwell's Relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

(from the expression for the Gibbs Free Energy) and the definition

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

, we have:

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

What we are really interested in is to find how $\triangle H_{evap} = H^{vap} - H^{liq}$ changes with temperature:

$$\left(\frac{\partial \Delta H_{evap}}{\partial P}\right)_T = \left(\frac{\partial\left[H^{vap} - H^{liq}\right]}{\partial P}\right)_T = \left(\frac{\partial H^{vap}}{\partial P}\right)_T - \left(\frac{\partial H^{liq}}{\partial P}\right)_T$$

$$\left(\frac{\partial \Delta H_{evap}}{\partial P}\right)_T = \left(V^{vap} - V^{liq}\right) - \left(V^{vap}\alpha^{vap} - V^{liq}\alpha^{liq}\right)T \approx V^{vap}\left(1 - \alpha^{vap}T\right)$$

In general, at relatively low pressures and densities, all gases behave ideally.

For an ideal gas, $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{PV} = \frac{1}{T}$ Therefore,

$$\left(\frac{\partial \Delta H_{evap}}{\partial P}\right)_T \approx 0$$

Problem 2.4

Given

$$U(S, X) = X^a \exp(bS)$$

First find the equations of state

$$T = \left(\frac{\partial U}{\partial S}\right)_X = X^a \exp(bs)b = bU(S, X)$$

$$f = \left(\frac{\partial U}{\partial X}\right)_S = aX^{a-1}\exp(bs) = \frac{aU(S, X)}{X}$$

From these we can derive the following which will be useful later

$$S = \frac{1}{b}\ln\left(\frac{T}{bX^a}\right) \tag{1}$$

$$\frac{T}{b} = \frac{fX}{a} \tag{2}$$

$$U(S, X) = \frac{T}{b} \tag{3}$$

$$X = \left[\frac{f}{a}\exp\left(-bS\right)\right]^{1-a} \tag{4}$$

Starting with the first function $D(S, f)$ we perform a Legendre transform as follows

$$D(S, f) = U - fX = (1 - a)U(S, X)$$

Now using (4) to get this in terms of S and f only

$$D(S, f) = (1 - a)\left[\frac{f}{a}\exp\left(-bS\right)\right]^{(1-a)a}\exp(bS)$$

Similarly for F(T,X)

$$F(T, X) = U - TS = U(S, X) - bU(s, x)S = (1 - bs)U(S, X)$$

Using (3) and (1) from above

$$F(T, X) = \left[1 - \ln\left(\frac{T}{bX^a}\right)\right]\frac{T}{b}$$

Now we do a transformation for to both T and f

$$K(T, f) = U - TS - fX$$

Using (3), (1) and (2)

$$K(T, f) = \frac{T}{b} - \frac{T}{b}\ln\left(\frac{T}{bX^a}\right) - \frac{Ta}{b}$$

$$K(T, f) = \frac{T}{b}\left[1 - a - \ln\left(\frac{T}{b\left(\frac{Ta}{bf}\right)^a}\right)\right]$$

Problem 2.5

(a) Start by using the chain rule on the left side of the equation

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

We know that $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ and we can expand the second derivative as follows

$$\left(\frac{\partial T}{\partial P}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T$$

Putting those together,

$$\frac{C_V}{T}\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T = -\frac{C_V}{T} * \left(\frac{1}{V\alpha}\right) * -V\beta$$

We can replace C_V by C_P using the relationship

$$C_P - C_V = \frac{TV\alpha^2}{\beta}$$

Yielding

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{\beta}{T\alpha}\left[C_P - \frac{TV\alpha^2}{\beta}\right] = \frac{C_P\beta}{T\alpha} - V\alpha$$

(b) We can expand the derivative as follows

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T$$

The first term is $\frac{T}{C_P}$ and the second term can be transformed using a Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. This gives

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\alpha V}{C_P}$$

(c) Start with the left side

$$T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = T\frac{\partial}{\partial T}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_V$$

Using a Maxwell relation,

$$T\frac{\partial}{\partial T}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_V = T\frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial V}\right)_T\right]_V = T\frac{\partial^2 S}{\partial T_V \partial V_T}$$

Now the right side

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V \rightarrow \left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial T}{\partial V}\right)_T\left(\frac{\partial S}{\partial T}\right)_V + T\frac{\partial}{\partial V}\left[\left(\frac{\partial S}{\partial T}\right)_V\right]_T$$

The first term in the above is zero since the change in temperature at constant temperature is zero. The second term can be written as

$$T\frac{\partial}{\partial V}\left[\left(\frac{\partial S}{\partial T}\right)_V\right]_T = T\frac{\partial^2 S}{\partial V_T \partial T_V}$$

And since we know the order of differentiation doesn't matter

$$T\frac{\partial^2 S}{\partial T_V \partial V_T} = T\frac{\partial^2 S}{\partial V_T \partial T_V}$$

Problem 2.6

(a) Start with the differential form of G

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial T}\right)_V = -S\left(\frac{\partial T}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial G}{\partial T}\right)_V = -S - V\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial T}\right)_V = -S - V\left(\frac{-1}{V\beta}\right)(V\alpha)$$

$$\left(\frac{\partial G}{\partial T}\right)_V = \frac{V\alpha}{\beta} - S$$

(b) Start with the differential form of H

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \frac{TC_P}{T}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

Problem 2.7

(For this problem Maple is our friend)

(a) This part involves taking the indicated derivatives of the given function. The two tricks are knowing what β is and how to change $\left(\frac{\partial U}{\partial V}\right)_T$ into something with derivatives of P w.r.t T or V.

$$\beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

and using the differential form of U and a Maxwell relation we get,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

The solutions are then

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\beta = \left(\frac{-1}{V}\right)\left(\frac{1}{\left(\frac{\partial P}{\partial V}\right)_T}\right) = \frac{(V-b)^2\,V^2}{RTV^3 - 2aV^2 + 4aVb - 2ab^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - P = \frac{a}{V^2}$$

(b)Remember

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha = \frac{R}{VP}$$

Expand H in differential form to try and get $\left(\frac{\partial H}{\partial P}\right)_T$ into a form you can solve for

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial T}\right)_T + V$$

$$\left(\frac{\partial H}{\partial P}\right) = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{-TR}{P} + V = b$$

Now for $C_P - C_V$

$$C_P - C_V = \frac{TV\alpha^2}{\beta}$$

$$C_P - C_V = \frac{R^3 T^2}{P^2(V-b)^2}$$

Problem 2.8

$$U = \frac{1}{k-1}PV + Nf\left(\frac{PV^k}{N^k}\right)$$

$$dU = TdS - PdV$$

For a reversible, adiabatic process,

$$(dU)_S = -P(dV)_S$$

Along a reversible adiabatic process: $PV^k = -g(S)$ so

$$P = -g(s)V^{-k}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P = g(s)V^{-k}$$

Again for a reversible, adiabatic process

$$(dU)_S = \left(\frac{\partial U}{\partial V}\right)_S dV = \frac{g(s)}{V^k}dV$$

Integrate from $V_0 \to V$ at constant S

$$U(V,S) - U(V_0,S) = \frac{-g(S)}{(k-1)}\left[\frac{1}{V^{k-1}} - \frac{1}{V_0^{k-1}}\right]$$

Moving things around,

$$U(V,S) = \left(\frac{-g(S)}{k}\frac{1}{V^{k-1}}\right) + \left[U(V_0,S) + \frac{g(S)}{(k-1)V_0^{k-1}}\right]$$

$$U(V,S) = \frac{-g(s)}{k-1}\frac{1}{V^{k-1}} + \underbrace{\left[U(V_0,S) + \frac{g(S)}{(k-1)V_0^{k-1}}\right]}$$

The second term above is only a function of S, so we can call it some function $w(S)$

$$U(V,S) = \frac{PV^k}{k-1}\frac{1}{V^{k-1}} + w(S) = \frac{PV}{(k-1)} + w(S)$$

$w(S)$ is an extensive function, therefore it can be written as N (the number of moles in the system) times a molar quantity $f(\underline{S})$

$$f\left(P\left(\frac{V}{N}\right)^k\right)$$

which is independent of the system size

$$U(V,S) = \frac{PV}{(k-1)} + Nf\left(P\frac{V^k}{N^k}\right)$$

Problem 2.9

The thermal expansivity is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Using a Maxwell relation,

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$$

And we are told in the problem that S is independent of crystallite structure and pressure, so

$$\left(\frac{\partial S}{\partial P}\right)_{T=0} = 0$$

And thus $\alpha = 0$ at absolute zero.

Problem 2.10

(a) The key property is that $\left(\frac{\partial S}{\partial H}\right)_T < 0$. This can be proven from the Maxwell relation.

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

(this can be proven from the differential of $d\phi = d(U - TS + PV - MH) = -SdT + VdP - MdH$) and since

$$\left(\frac{\partial M}{\partial T}\right)_H < 0 \implies \left(\frac{\partial S}{\partial H}\right)_T < 0$$

$S(T)$ as constant H therefore has the following shape.

Adiabatic demagnetization consists of two steps:
    I. Isothermal application of a field
    II. insulate material and turn off the field $\rightarrow$ isotropic demagnetization. System moves back to state with $H = 0$, hence T decreases.

(b)

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{\left(\frac{\partial S}{\partial H}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_H} = -\frac{\left(\frac{\partial M}{\partial T}\right)_H}{\frac{c_H}{T}}$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{c_H}$$

We can evaluate $\left(\frac{\partial M}{\partial T}\right)_H$ as follows

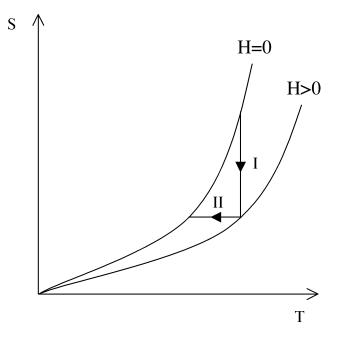$$M = \frac{\kappa V}{T}H \implies \left(\frac{\partial M}{\partial T}\right)_H = -\frac{\kappa V}{T^2}H$$

Figure 1:

So,

$$\boxed{\left(\frac{\partial T}{\partial H}\right)_S = \frac{\kappa V H}{c_H T}}$$

LEVEL 3 PROBLEMS

Problem 3.1

Given:

$$\underline{U} = \left(\frac{\theta}{R}\right)\underline{S}^2 - \left(\frac{R\theta}{V_0^2}\right)\underline{V}^2$$

(a) We want to make this the absolute U and not the molar quantity, so multiply by N.

$$U = N\underline{U} = \left(\frac{N\theta}{R}\right)\underline{S}^2 - \left(\frac{NR\theta}{V_0^2}\right)\underline{V}^2 = \left(\frac{N\theta}{R}\right)\left(\frac{S}{N}\right)^2 - \left(\frac{NR\theta}{V_0^2}\right)\left(\frac{V}{N}\right)^2$$

$$U = \frac{1}{N}\left[\left(\frac{\theta}{R}\right)S^2 - \left(\frac{R\theta}{V_0^2}\right)V^2\right]$$

The equations of state give us

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V} = \frac{2}{N}\left(\frac{\theta}{R}\right)S$$

$$P = \left(\frac{\partial U}{\partial V}\right)_{N,S} = \frac{2}{N}\left(\frac{R\theta}{V_0^2}\right)V$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{P,S} = -\frac{1}{N^2}\left[\left(\frac{\theta}{R}\right)S^2 - \left(\frac{R\theta}{V_0^2}\right)V^2\right] = -\left[\left(\frac{\theta}{R}\right)\underline{S}^2 - \left(\frac{R\theta}{V_0^2}\right)\underline{V}^2\right]$$

or

$$\mu = -\underline{U}$$

(b) Express μ as a function of T and P

$$S = \frac{N}{2}\left(\frac{R}{\theta}\right)T$$

$$V = -\frac{N}{2}\left(\frac{V_0^2}{R\theta}\right)P$$

Substitute in to the expression for μ

$$\mu = -\frac{1}{N^2}\left[\left(\frac{\theta}{R}\right)\frac{N^2}{4}\left(\frac{R}{\theta}\right)^2 T^2 - \left(\frac{R\theta}{V_0^2}\right)\frac{N^2}{4}\left(\frac{V_0^2}{R\theta}\right)^2 P^2\right]$$

$$\mu = -\left[\frac{1}{4}\left(\frac{R}{\theta}\right)T^2 - \frac{1}{4}\left(\frac{V_0^2}{R\theta}\right)P^2\right]$$

Problem 3.2

Start with the expression we used in class

$$\left(\frac{\partial x}{\partial f}\right)_z = \left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f\left(\frac{\partial y}{\partial f}\right)_z$$

For this problem, this equation can relate the constant l heat capacity to the constant P heat capacity as follows,

$$\left(\frac{\partial S}{\partial T}\right)_l = \left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_l$$

To get heat capacity we need to multiply both sides by T, and when we do this we get

$$C_l = C_p + T\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_l$$

The first derivative can be rewritten using the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ which simplifies to

$$C_l = C_p - T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_l$$

And since we know that $\left(\frac{\partial V}{\partial T}\right)_P = V\alpha$

$$C_l = C_p - TV\alpha\left(\frac{\partial P}{\partial T}\right)_l$$

Now we need to expand the second derivative

$$\left(\frac{\partial P}{\partial T}\right)_l = -\left(\frac{\partial P}{\partial l}\right)_T \left(\frac{\partial l}{\partial T}\right)_P$$

Since the material is isotropic, $\left(\frac{\partial l}{\partial T}\right)_P = \frac{1}{3}V\alpha$ which now leave us with

$$C_l = C_p + \frac{1}{3}TV^2\alpha^2\left(\frac{\partial P}{\partial l}\right)_T$$

One more partial to go....if we look at the relationship between stress and strain,

$$\sigma = E\varepsilon \text{ and thus } \left(\frac{\partial \sigma}{\partial \varepsilon}\right)_T = E$$

where E is the Young's modulus for an isotropic material. To get this in a form we can use, we need to multiply by l to switch from $\partial\varepsilon$ to ∂l and then invert. This then will give us

$$C_l = C_p + \frac{1}{3}\frac{TV^2\alpha^2 E}{l}$$

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Problem 3.3

</div>

The total system is at constant volume and temperature hence its Helmholtz free energy is minimal with respect to the internal degrees of freedom.
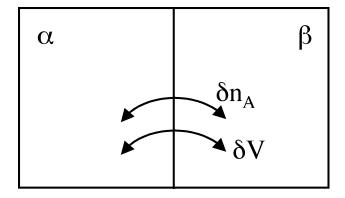

Figure 2:

$$dF^{tot} = dF^\alpha + dF^\beta$$

$$dF^{tot} = -S^\alpha dT^\alpha - p^\alpha dV^\alpha + \mu_A^\alpha dn_A^\alpha - S^\beta dT^\beta - p^\beta dV^\beta + \mu_A^\beta dn_A^\beta$$

since $dT^\alpha = dT^\beta = 0$ and $dV^\alpha = -dV^\beta$ and $dn_A^\alpha = -dn_A^\beta$ we can write

$$dF^{tot} = -\left(p^\alpha - p^\beta\right) dV^\alpha + \left(\mu_A^\alpha - \mu_A^\beta\right) dn_A^\alpha$$

If dV^α and dn_A^α were independent, equilibrium would require that $p^\alpha = p^\beta$ and $\mu_A^\alpha = \mu_A^\beta$. However dV^α and dn_A^α are NOT independent!

$$dV^\alpha = K dn_A^\alpha$$

$$dF^{tot} = \underbrace{\left(\frac{\mu_A^\alpha - \mu_A^\beta}{K} - \left(p^\alpha - p^\beta\right)\right)}_{} dV^\alpha$$

The bracketed term must equal zero for equilibrium.

$$\boxed{\mu_A^\alpha - Kp^\alpha = \mu_A^\beta - Kp^\beta}$$

Problem 3.4

The heat capacity c_x is related to the temperature derivative of the entropy under the condition x. (x being the conditions defined in the problem statement)

$$c_x = T\left(\frac{\partial S}{\partial T}\right)_x$$

Starting with $S(T, P)$ we write

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

We can take the temperature derivative of this holding x constant

$$\frac{\partial}{\partial T}\left(dS\right)_x = \frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP\right]_x$$

$$\left(\frac{\partial S}{\partial T}\right)_x = \frac{c_p}{T} + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_x$$

(Note: The above can also be obtained using $\left(\frac{\partial x}{\partial f}\right)_z = \left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z$)

We know through a Maxwell relation that $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha_v V$. So now we need to find $\left(\frac{\partial P}{\partial T}\right)_x$. We start from the given information that $V - aP = $ a constant, thus $dV = adP$. This gives us

$$\left(\frac{\partial P}{\partial T}\right)_x = \frac{1}{a}\left(\frac{\partial V}{\partial T}\right)_x$$

Continuing from there, we write out the differential form of $V(T, P)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

But we know $\left(\frac{\partial V}{\partial T}\right)_P = \alpha_v V$ and $\left(\frac{\partial V}{\partial P}\right)_T = -\beta_T V$. We now have

$$dV = \alpha_v V\, dT + -\beta_T V\, dP$$

So $\left(\frac{\partial V}{\partial T}\right)_x$ is given by

$$\left(\frac{\partial V}{\partial T}\right)_x = \alpha_v V - \beta_T V\left(\frac{\partial P}{\partial T}\right)_x$$

Replacing $\left(\frac{\partial P}{\partial T}\right)_x$ we get

$$\left(\frac{\partial V}{\partial T}\right)_x = \alpha_v V - \frac{\beta_T V}{a}\left(\frac{\partial V}{\partial T}\right)_x$$

or

$$\left(\frac{\partial V}{\partial T}\right)_x = \frac{\alpha_v V a}{a + \beta_T V}$$

Putting this all together...

$$\left(\frac{\partial S}{\partial T}\right)_x = \frac{c_p}{T} + (-\alpha_v V)\left(\frac{1}{a}\right)\left(\frac{\partial V}{\partial T}\right)_x$$

$$\left(\frac{\partial S}{\partial T}\right)_x = \frac{c_p}{T} + (-\alpha_v V)\left(\frac{1}{a}\right)\left(\frac{\alpha_v V a}{a + \beta_T V}\right)$$

$$T\left(\frac{\partial S}{\partial T}\right)_x = c_p + T(-\alpha_v V)\left(\frac{1}{a}\right)\left(\frac{\alpha_v V a}{a + \beta_T V}\right)$$

So we get finally that

$$\boxed{c_x = c_p - \frac{T(\alpha_v V)^2}{a + \beta_T V}}$$