Problem 7.2 [FOR ASSIGNMENT 4; max 10 points]
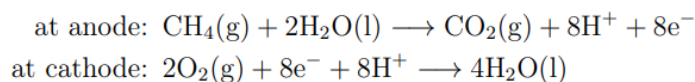
Methane fuel cell.

The chemical reaction for a methane fuel cell is described below:

$$\text{at anode: } CH_4(g) + 2H_2O(l) \longrightarrow CO_2(g) + 8H^+ + 8e^-$$
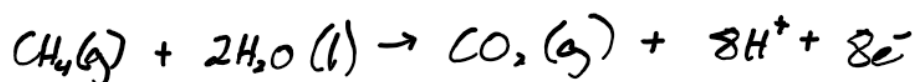$$\text{at cathode: } 2O_2(g) + 8e^- + 8H^+ \longrightarrow 4H_2O(l)$$

(a) Determine $\mathcal{E}_0$, the voltage of the cell at normal conditions (room temperature and atmospheric pressure).

(b) Estimate how the voltage depends on T at constant P, that is, find the derivative $\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$.

(c) Assuming ideal performance, how much electrical work can you get out of the cell for each mole of methane (CH_4)?

(d) Estimate the amount of heat released to the environment or absorbed by the fuel cell for each "burned" mole of methane.
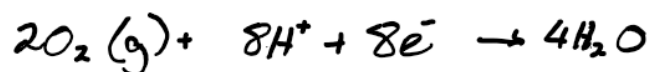
a)   Normal conditions:

$$P = 101.325 \, kPa$$
$$T = 293.15 \, K$$

$$\mathcal{E}_0 = -V_{anode} + V_{cathode}$$

At anode:

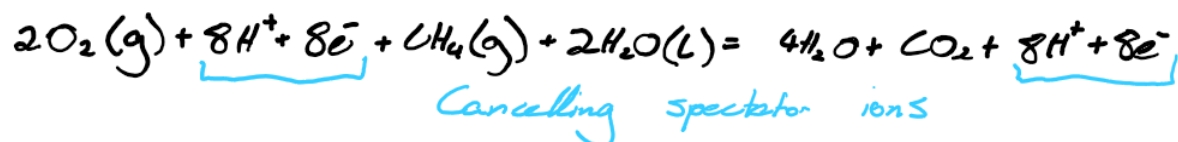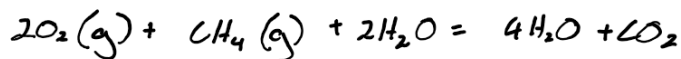$$CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+ + 8e^-$$

And cathode:

$$2O_2(g) + 8H^+ + 8e^- \rightarrow 4H_2O$$

Thus we see the total equation:

$$2O_2(g) + 8H^+ + 8e^- + CH_4(g) + 2H_2O(L) = 4H_2O + CO_2 + 8H^+ + 8e^-$$

Cancelling spectator ions

$2O_2(g) + CH_4(g) + 2H_2O = 4H_2O + CO_2$

We first realize that the voltage of such a cell is given by:

$$\varepsilon_0 = \frac{|\Delta G_m|}{n N_A |q_e|}$$ where n is the number of moles of electrons transferred

Thus

$$\varepsilon_0 = \frac{|\Delta H - T\Delta S|}{8 N_A |q_e|}$$

From the chemical equation we understand:

$$\Delta S = \underbrace{4 S(H_2O) + S(CO_2)}_{\text{Final entropy}} - \underbrace{\left(2 \times S(O_2) + S(CH_4) + 2 S(H_2O)\right)}_{\text{Initial entropy}}$$

Final entropy — Initial entropy

From the formula sheet:

$\Delta S = 4 \times 69.91 + 213.75 - 2 \times 205.14 - 186.26 - 2 \times 69.91$

$= -242.97$ J/k

And:

$\Delta H = 4 \ H(H_2O) + H(CO_2) - \left(2 \times H(O_2) + H(CH_4) + 2H(H_2O)\right)$

Note all H values were relative and taken from the formula sheet.

$\Delta H = 4 \times -285.83 + -393.51 - \left(2 \times 0 + -74.81 + 2 \times -285.83\right)$

$= -889.36$ kJ

$\therefore \quad \varepsilon_0 = \frac{|\Delta H - T\Delta S|}{8 \times 6.02 \times 10^{23} \times 1.6 \times 10^{-19}}$

$= \frac{|-889.36 \times 10^3 - 293.15 \times -242.97|}{8 \times 6.02 \times 10^{23} \times 1.6 \times 10^{-19}}$

$= \frac{818133.34}{770560} = 1.062V$

b) We understand:

$$\varepsilon = \frac{|\Delta H - T \Delta S|}{n N_A |q|}$$

We know the values for ΔH and ΔS thus:

$$\varepsilon = \frac{|-889.36 \times 10^3 + 242.97 T|}{770560}$$

$$= \frac{889.36 \times 10^3 - 242.97 T}{770560}$$

$$= 1.15 - 0.0003 T$$

$$\left(\frac{\partial \varepsilon}{\partial T}\right)_p = \frac{\partial}{\partial T}\left(1.15 - 0.0003 T\right)$$

$$= -0.0003$$

c) For one mole of methane we can find the electrical work by envoking Gibbs free energy change. The work done other than expansion:

$$\Delta G = \Delta H - T \Delta S$$

One mole of CH_4 results in

$$\Delta H = - 889.36 \text{ kJ}$$

$$\Delta S = -242.97 \text{ J/k}$$

Thus at room temp, the electrical work acheived by the cell is:

$$\Delta G = - 889.36 \times 10^3 + 242.97 \times 293.15$$
$$= - 818133.3 \text{ J}$$

Electrical work = 818133.3 J

d) We understand that at constant pressure,

$$Q_p = \Delta H \quad \text{and Thus:}$$

$$Q_p = \Delta G + T \Delta S$$
$$= - 818133.3 + 293.15 \times - 242.97$$
$$= - 889359.96 \text{ J}$$

Thus 889359.96 J of heat was released to the environment.

Problem 7.5   [FOR ASSIGNMENT 4; max 10 points]

The Joule-Thomson process.

Throttling (also known as the Joule-Thomson process) is an isenthalpic process by which a fluid is compressed through a valve or porous plug and expands into a lower pressure chamber (the valve / plug ensures the flow is slow enough to keep the pressure of the two chambers roughly constant, yet mutually unequal, as the volume within each chamber changes).

For an ideal gas, such a process would result in no change in temperature: since the gas particles do not interact, $H \equiv H(T)$ and hence $\Delta T = 0$. However, for real gases, there are such interactions, which leads to a dependence between temperature and pressure. This dependence is characterised by the **Joule-Thomson coefficient**:

$$\mu_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1), \tag{1}$$

where $\alpha = V^{-1}(\partial V/\partial T)_P$ is the isobaric thermal expansion coefficient.

In this question, you will derive the Joule-Thomson coefficient from Equation 1, and explore certain related effects.

(a) By using the triple product rule on T, P and H, show that

$$\mu_{\mathrm{JT}} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P}.$$

   HINT: for partial derivatives, $\left(\frac{\partial x}{\partial y}\right)_z = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]^{-1}$.

(b) Show from the thermodynamic identity for H that

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

   and then using an appropriate Maxwell relation, show that

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

   HINT: recall that $\alpha = V^{-1}(\partial V/\partial T)_P$. You may also find Problem 7.4 helpful here.

(c) Using the fact that $C_P = (\partial H/\partial T)_P$ and the results from parts (a) and (b), obtain the result from Equation 1.

(d) Since the temperature of an ideal gas is constant for all isenthalpic processes, what is μ_{JT} for an ideal gas? From this, determine the equation for α of an ideal gas as a function of T.

(e) The Joule-Thomson coefficient of real gases can be positive or negative depending on the initial temperature of the gas. The temperature at which μ_{JT} switches signs is called the *inversion temperature*. What happens to a gas that is throttled if $\mu_{\mathrm{JT}} > 0$? What about $\mu_{\mathrm{JT}} < 0$? Given this—and with explicit reference to the inversion temperature and μ_{JT}—why do you think hydrogen, helium and neon cannot be cooled by throttling at room temperature, but all other gases can?

a) We first take the identity:

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

First, at constant T:

$$\frac{\partial H}{\partial P} = \frac{\partial}{\partial P}\left(TdS + VdP + \mu N\right)$$

$$= V$$

Now constant P:

$$\frac{\partial H}{\partial T} = \frac{\partial}{\partial T}\left(TdS + VdP + \mu N\right)$$

$$= dS$$

Now we notice:

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

Which given:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial}{\partial P}\left(\frac{dH}{dS} - \frac{VdP}{dS} - \frac{\mu dN}{dS}\right)$$

$$= \frac{\partial}{\partial P}\frac{-VdP}{dS} = \frac{-V}{dS}$$

Thus we have shown

$$\mu_{JT} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \qquad QED$$

b) $H = u + PV$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(u + PV\right)$$

Given at constant T:
$$W = \Delta F + T\Delta S - Q$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\Delta F + T\Delta S - Q + PV\right)$$

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

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

We now recall the maxwell relation:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad \textcircled{1}$$

Thus:

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

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

$$= -V\left(\alpha T - 1\right)$$

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

QED

c) Given $C_p = \left(\dfrac{\partial H}{\partial T}\right)_P$ and that

we have previously shown:

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

We observe:

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

And since:

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

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

QED

d) First starting with:

$$\left(\frac{\partial H}{\partial P}\right)_T \quad \text{as } H \text{ and } T \text{ are both constant:}$$

$$= \frac{\partial}{\partial P}\left(U + PV\right) \quad \underset{\curvearrowleft}{\bigg)} U = 0$$

$$= V$$

Thus:

$$V = -v(\alpha T - 1)$$

$$1 = -(\alpha T - 1)$$

$$0 = \alpha T$$

And given T is constant,

$$\alpha = 0$$

E)

When the value for μ_{JT} is negative, it is implied that an increase in pressure will result in a decrease of temperature, and when positive, an increase in pressure will result in an increase in temperature. This implies that when throttled, positive μ_{JT} warms, and negative cools. For the gases hydrogen, helium and neon, I suspect that given their inversion temperatures when looked up online are below room temperature (200K, 40K and 45K respectively), when throttled at room temperature, they will always heat up. Assuming most other gases have inversion temperatures above 293K, they will cool down upon throttling, resulting in a drop in pressure without external energy loss as intended in a throttling process.

Problem 8.4 [FOR ASSIGNMENT 4; max 10 points]

Thermodynamic properties of pure substance phase transitions.

(a) Why is the change of entropy almost always positive when a substance evaporates and when it melts?

(b) A well-known counterexample to the statement in part (a) is helium-3. At pressures above $P \approx 29$ atm and temperatures below $T \approx 0.3$ K, the entropy actually *decreases* when it melts due to unique quantum interactions between the spins of the individual nuclei. A phase diagram for ^{3}He is provided in Figure 2.

Given that $S_{\text{liq}} < S_{\text{sol}}$, and as with most substances $v_{\text{liq}} > v_{\text{sol}}$ (with v specific volume), can you devise a method to cool ^{3}He via compression along the liquid-solid coexistence curve?

HINT: consider the phase diagram in Figure 2 and use the Clausius-Clapeyron relation. This effect is known as *Pomeranchuk cooling*, and was pivotal to the 1996 Nobel physics prize for the discovery of superfluidity in ^{3}He.

(c) Figure 3 shows a hypothetical PT phase diagram. This phase diagram is not possible for a pure substance. Describe all the features of the diagram that will not be observed or are extremely rare.

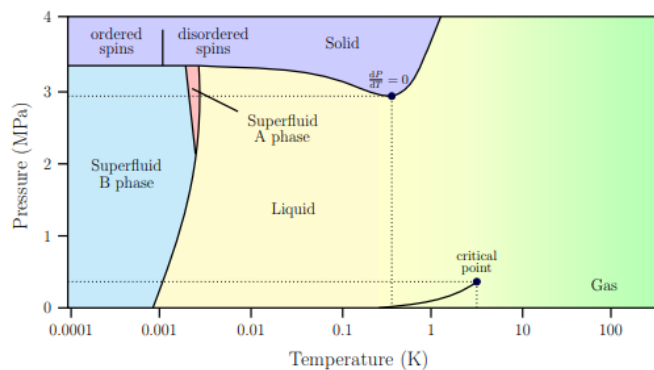HINT: You should describe four different features.

Figure 2: Phase diagram for ^{3}He. Note that at 29 atm and 0.3 K, $dP/dT = 0$. This means, for example, that if helium-3 is heated at 30 atm from 0.01 K to 1 K, the phase transitions from liquid, to solid, then back to liquid. This is due to the liquid phase of ^{3}He having less entropy than the solid phase when $P > 29$ atm and $T < 0.3$ K. The x-axis is logarithmically scaled.
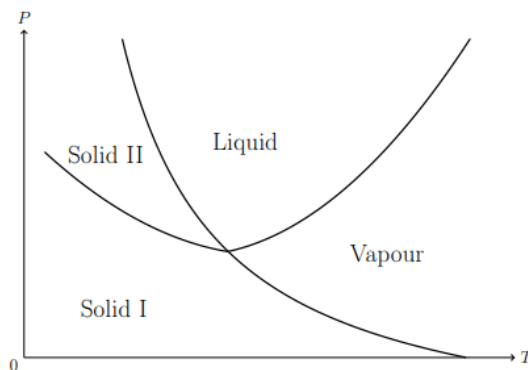

Figure 3: A hypothetical phase diagram of a pure substance. Solid I and Solid II are two types of its crystal structure. The x-axis uses an absolute temperature scale.

A)

As a pure substance melts or evaporates, the molecules are transitioned from a more to less uniform state, in other words, the number of microstates in the macrostate increases. We directly understand the implication this has on entropy as:

$$S = k\ln(\Omega)$$

Where Ω is the number of different microstates. This could further be related to the latent heat of fusion and vaporisation for melting and evaporating respectively. As phase transition requires some amount of added heat, during which the temperature is unchanged as the heat is used to break/create bonds as opposed to increase kinetic energy, we notice from the thermodynamic identity for G:

$$\Delta G = 0 = \Delta H - T\Delta S \qquad \therefore \quad \Delta S = \frac{\Delta H}{T}$$

No work done

Thus, we have shown that ideally, no work done by the system during transition outlined the entropies dependence on enthalpy change, which will increase during transition as heat must be added, thus directly implying the increase in different microstates as enthalpy increases.

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

From along the solid-liquid line for helium-3 we find:
T increases as the spins become more ordered.
Based on the Clausius-Clapeyron equation:

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

↙ — Slope of the solid-liquid coexistance curve

Given $S_{liq} < S_{sol}$, $V_{liq} > V_{sol}$

We notice:

$$\frac{dP}{dT} = \frac{S_{liq} - S_{sol}}{V_{liq} - V_{sol}} = \frac{L}{T\Delta V} < 0$$

↗ +ve

↙ -ve

↖ ΔV must be -ve.

Thus we have shown that compression along the liquid-solid curve will increase the pressure thus decreasing the temperature as:

$$\frac{dP}{dT} = \frac{L}{T\Delta V} < 0$$

In other words:
$\Delta V < 0$ leads to
$\frac{dP}{dT} < 0$ and $dP > 0$
and thus $dT < 0$

C)

We understand the PT curve will have non-valid features should they violate conditions of equilibrium.

1. The first violated condition occurs when the pressure drops to 0 whilst having a non-zero temperature. This directly violated PV = nRT as we would find 0 = nRT with nRT being non-zero. The liquid-vapor line continues indefinitely whilst it should hit a point of criticality.
2. The second violating feature is the concave characteristic of the solid-solid boundary. Given solid 2 occurs at a higher pressure, a little curved upwards down in order to preserve correct entropy transformations.
3. Thirdly the diagram only has one triple point, at which two solids, the liquid and the vapor meet. It is extremely rare for a vapor to have a triple point with two different solids.
4. Finally, the liquid phase is more stable at high pressures than both the solid phases, whilst for pure substances specifically, the solids is commonly stable at high pressures.

Problem 8.6 [FOR ASSIGNMENT 4; max 10 points]

Properties of thermodynamically stable phases.

A substance is split into two halves as shown in Figure 5. The separating piston can move left and right without any friction with the walls of the container. The volume of the container and the temperature are fixed. Consider a rapid movement of the piston away from its initial equilibrium position so that the volume on one side of the piston decreases by a very small amount, and the volume on the other side increase by this same small amount.

(a) Write the Taylor series of the Helmholtz potential $F(T,V)$ at fixed T for the split substance in each half of the container. Then derive an expression for the change of $F(T,V)$ for the whole system when the piston moves, up to the second order terms.

HINT: Although the total volume of the container is fixed, the volumes in each half are not.

$$V, T = \text{constant}; \quad V = V_{\text{L}} + V_{\text{R}}$$

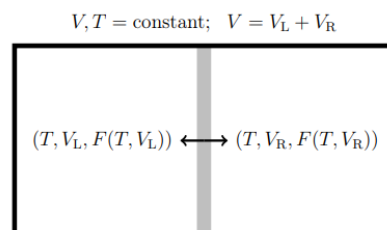$$(T, V_{\text{L}}, F(T, V_{\text{L}})) \longleftrightarrow (T, V_{\text{R}}, F(T, V_{\text{R}}))$$

Figure 5: A piston (grey bar) splits the container (black rectangle) completely filled with a substance into two parts. The piston can move left and right without any friction with the container. The volume and the temperature of the container are fixed.

(b) Use the condition of thermodynamic equilibrium of the entire system at constant temperature and volume to show that $(\partial^2 F/\partial V^2)_T > 0$ should hold at equilibrium.

HINT: See problem 8.5(a). A movement of the piston should push the system away from equilibrium.

(c) Use the result obtained in part (b) to prove that $(\partial P/\partial V)_T < 0$.

(d) In most cases, a thermal expansion coefficient is positive, however this is not generally true. A unique but well-known counterexample is water between 0°C and 4°C where $\left(\frac{\partial V}{\partial T}\right)_P < 0$.

The volume of an ideal gas at constant temperature decreases if the pressure on it increases. Do you think there could be a unique but thermodynamically stable substance such that its volume at constant temperature will increase if the pressure increases? Explain your answer.

Helmholtz states:

$$F = u - TS$$

For the left half we find:

$$T = T \qquad V_L = V - V_R$$

The total free energy of the system F is the sum of the left and right sides:

$$F(T, V) = F_L(T, V_L) + F_R(T, V_R)$$

Initially we understand:

$$V_L = V_R = \frac{V}{2}$$

As the piston moves left, V_L decreases:

$$\delta V_L = \frac{V}{2} - \delta V \qquad\qquad V_R = \frac{V}{2} + \delta V$$

We notice at these points:

$$F_L\left(T, \frac{V}{2} - \delta V\right) \qquad\qquad F_R\left(T, \frac{V}{2} + \delta V\right)$$

This can be expanded using the Taylor series given T is constant.
(About equilibrium)

$$F_L\left(T, \frac{V}{2} - \delta V\right) = F_L\left(T, \frac{V}{2}\right) - \delta V \frac{\partial F_L}{\partial V} + \frac{1}{2}(\delta V)^2 \frac{\partial^2 F_L}{\partial V^2}$$

$$F_R\left(T, \frac{V}{2} + \delta V\right) = F_R\left(T, \frac{V}{2}\right) + \delta V \frac{\partial F_R}{\partial V} + \frac{1}{2}(\delta V)^2 \frac{\partial^2 F_R}{\partial V^2}$$

Thus given $F_T(T, V) = F_L(T, V_L) + F_R(T, V_R)$ we find:

$$\Delta F_T(T, v) = \Delta F_L + \Delta F_R - 2F_i$$

Free energy
initially in each side:

$$= F_L\left(T, \frac{v}{2}\right) - \delta v \frac{\partial F_L}{\partial v} + \frac{1}{2}(\delta v)^2 \frac{\partial^2 F_L}{\partial v^2}$$

$$+ F_R\left(T, \frac{v}{2}\right) + \delta v \frac{\partial F_R}{\partial v} + \frac{1}{2}(\delta v)^2 \frac{\partial^2 F_R}{\partial v^2}$$

$$- 2F_L\left(T, \frac{v}{2}\right)$$

$$= 2 \times \frac{1}{2}(\delta v)^2 \frac{\partial^2(F_L + F_R)}{\partial v^2}$$

$$\Delta F(T, v) = (\delta v)^2 \frac{\partial^2 F}{\partial v^2}$$

b) We understand that at equilibrium
Free energy (F) is at a minimum.
This implies $\Delta F > 0$ must always
be true as otherwise the system
is not in equilibrium.
We also notice that regardless of
the δV sign, $(\delta V)^2$ is always
positive.

Thus as:

$$\Delta F > 0 \implies (\delta V)^2 \frac{d^2 F}{dv^2} > 0$$

and as $(\delta V)^2 > 0$

we have shown $\frac{d^2 F}{dv^2} > 0$

c) To prove $\frac{dP}{dT} < 0$ we first use:

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

Given constant T and N:

$$dF = -PdV$$

$$\frac{dF}{dV} = -P \qquad \text{now taking } \frac{d}{dV}$$
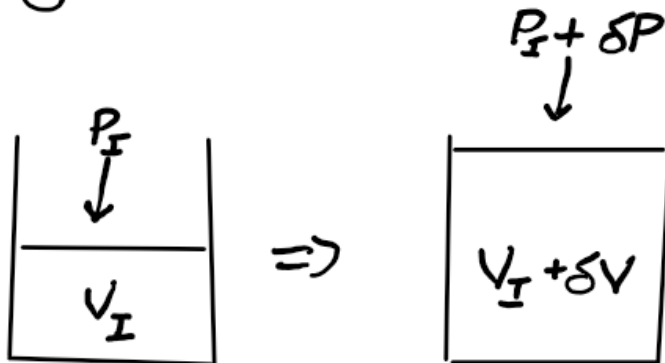$$\text{of both sides:}$$

$$\frac{d^2F}{dV^2} = -\frac{dP}{dV}$$

Now since $\frac{d^2F}{dV^2} > 0$, $\frac{dP}{dV}$ must

be less than 0 i.e :

$$\left(\frac{dP}{dV}\right)_T < 0$$

d) We aim to show an example of
Volume increase if pressure on the
system increases at constant temp.

$$P_I + \delta P$$
$$\downarrow$$

We have shown that:

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad \text{and thus} \quad \left(\frac{\partial V}{\partial P}\right) < 0$$

must also be true.

We know this result is true as
if $\left(\frac{\partial V}{\partial P}\right) < 0$ then $\left(\frac{\partial P}{\partial V}\right) < 0$

and thus $\frac{d^2 F}{d V^2} < 0$. For an

equilibrium state, the free energy
cannot decrease and thus $\frac{d^2 F}{d V^2} < 0$

Cannot be true as the concavity of
F and convexity of entropy is
violated. Thus $\frac{\partial P}{\partial V} < 0$

can never be physically realised.