3.20 Exam 1
Fall 2003
SOLUTIONS

Question 1

You need to decide whether to work at constant volume or constant pressure. Since F is given, a natural choice is constant volume.

Option 1:
At constant T and V:
$$dF = -SdT - PdV + HdM$$

H is a *derived quantity* in the Helmholtz free energy representation of this magnetic system and we therefore have:

$$H \equiv \left(\frac{\partial F}{\partial M} \right)_{T,V}$$

Given that the Helmholtz free energy of this system is expressed as:

$$F = A \left(\frac{M}{\mu} - \frac{1}{2} \right)^2$$

We finally have:

$$H = \frac{2A}{\mu} \left(\frac{M}{\mu} - \frac{1}{2} \right)$$

Option 2:
If you chose to work at constant pressure instead, you need to start with the Gibbs free energy:
At constant T and P:

$$G = U - TS + PV$$
$$dG = -SdT + VdP + HdM$$

Again, H in this a derived quantity in the Gibbs free energy representation for this magnetic system and we have:

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

Using the definition of the Gibbs free energy, we have:

$$G = F + PV = A \left(\frac{M}{\mu} - \frac{1}{2} \right)^2 + PV$$

and finally we have:

$$H = \frac{2A}{\mu} \left(\frac{M}{\mu} - \frac{1}{2} \right) + P \left(\frac{\partial V}{\partial M} \right)_{T,P}$$

Note that $H(M)$ obtained from F agrees with $H(M)$ obtained from G when V is constant, since the term $\left(\frac{\partial V}{\partial M}\right)$ disappears.

Question 2

a)

Under constant P and T conditions, the relevant potential for this system is the Gibbs free energy:

$$dG = -SdT + VdP$$

Since $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $V_\alpha < V_\beta$, the free energy of the β phase can be lowered relative to that of α by applying pressure.

b)

The change in the Gibbs free of transformation $\alpha \to \beta$ is given by:

$$\Delta G^{\alpha \to \beta}(T) \approx \Delta H \left(1 - \frac{T}{T_0}\right)$$

At constant temperature, the change in the Gibbs free energy of transformation with pressure is given by:

$$\left.\frac{\partial G}{\partial P}\right)_T = V \to \frac{\partial \Delta G^{\alpha \to \beta}}{\partial P}\right) = \Delta V^{\alpha \to \beta}$$

To find the work absorbed from the environment, it is necessary first to find the transition pressure, P^*, at $300\ K$:

$$\Delta G(P, 300K) = \Delta G(1, 300K) + P\Delta V^{\alpha \to \beta}$$

Since, at the transition pressure, P^*, and temperature ($300\ K$), $\Delta G^{\alpha \to \beta} = 0$,

$$P^* = -\frac{\Delta G(1, 300K)}{\Delta V^{\alpha \to \beta}}$$

The amount of work absorbed by the environment is given by:

$$Work = -\int P^* dV = -P^* \Delta V^{\alpha \to \beta} = \Delta G(1, 300K)$$

At $300K$,

$$\Delta G(1, 300K) = \Delta H \left(1 - \frac{T}{T_0}\right) = \left(1000^J/_{mol}\right)\left(1 - \frac{300}{350}\right)$$

$$Work = 143^J/_{mol}$$

c)

In this case, the system undergoes a phase transition at constant pressure and entropy. The relevant potential is H, enthalpy.

It is necessary, as before, to find the pressure at which the transition occurs, under this adiabatic condition. The equilibrium condition in this case is given by:

$$H^\alpha (S, P^*) = H^\beta (S, P^*)$$

Need to find $P*$ for which $\triangle H(P^*) = 0$

$$\left(\frac{\partial \Delta H}{\partial P} \right)_S = \Delta V \to P^* = -\frac{\Delta H (P = 1)}{\Delta V}$$

The work absorbed by the environment is then given by:

$$Work = - \int P^* dV = -P^* \Delta V^{\alpha \to \beta} = \Delta H (1) = 1 kJ/mol$$

Question 3

a)

In this problem, given a fundamental equation of the internal energy of a system as a function of extensive properties, you were asked to find the three relevant equations of state, in this case, T, $-P$ and μ.

From the expression for the first law:

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

and using

$$U = \frac{AS^3}{NV}$$

The three equations of state are:

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{3AS^2}{NV}$$

$$-P \equiv \left(\frac{\partial U}{\partial V}\right)_{S,N} = -\frac{AS^3}{NV^2}$$

$$\mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V} = -\frac{AS^3}{N^2V}$$

b)

In order to prove that the equations of state obtained in part $a)$ are intensive properties, i.e. their value does not depend on the size of the system, we need to prove the following:

$$Y(\lambda S, \lambda V, \lambda N) = Y(S, V, N)$$

where Y is an intensive property of a thermodynamic system or an equation of state from the internal energy representation of the first law.

For this particular problem,

$$T = \frac{3A(\lambda S)^2}{(\lambda N)(\lambda V)} = \frac{\lambda^2 3AS^2}{\lambda^2 NV} = \frac{3AS^2}{NV}$$

$$-P = -\frac{A(\lambda S)^3}{(\lambda N)(\lambda V)^2} = -\frac{\lambda^3 AS^3}{\lambda^3 NV^2} = -\frac{AS^3}{NV^2}$$

$$\mu = -\frac{A(\lambda S)^3}{(\lambda N)^2(\lambda V)} = -\frac{\lambda^3 AS^3}{\lambda^3 N^2V} = -\frac{AS^3}{N^2V}$$

Question 4

Note that the heat capacity for this system is neither C_P nor C_V since the volume and pressure inside the bubble are *not* constant upon heating.

Heat capacities, in general, are defined by $C_X = T\left(\frac{\partial S}{\partial T}\right)_X$. In this problem, it is necessary to find the condition X that remains constant and which is not V or P.

For a simple system, it is possible to express the change in entropy as a function of (T, P):

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

It is possible to take the partial derivative of the above expression, with constant X:

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

Note that this looks like the 'Zemansky Rule'.

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

To find C_X as a function of known properties of the system, it is necessary to manipulate the expression above.

We start by using a Maxwell Relation to find (considering an ideal gas):

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

$$C_X = C_P - V \left(\frac{\partial P}{\partial T}\right)_X$$

Need to find $\left(\frac{\partial P}{\partial T}\right)_X$.

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

To find dX, we use the condition for mechanical equilibrium between the gas inside the bubble and the environment:

$$P_i = P_o + \frac{2\sigma}{r}$$

$$dP_i - \frac{2\sigma}{r^2} dr = 0$$

$$V = \frac{4}{3}\pi r^3 \rightarrow dV = 4\pi r^2 dr$$

$$dP - \frac{2}{3}\frac{\sigma}{r}\frac{dV}{V} = 0$$

$$\left(\frac{\partial P}{\partial T}\right)_X = -\frac{\left(\frac{\partial P}{\partial T}\right)_P - \frac{2\sigma}{3rV}\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial P}\right)_T - \frac{2\sigma}{3rV}\left(\frac{\partial V}{\partial P}\right)_T} = -\frac{0 - \frac{2\sigma}{3rV}\left(\frac{\partial V}{\partial T}\right)_P}{1 - \frac{2\sigma}{3rV}\left(\frac{\partial V}{\partial P}\right)_T}$$

For an ideal gas,

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

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{NR}{PV} = \frac{1}{T} \quad \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-NRT}{P^2V} = -\frac{1}{P}$$

$$\left(\frac{\partial P}{\partial T}\right)_X = \frac{+\frac{2\sigma}{3rT}}{1 - \frac{2\sigma}{3rP}}$$

The specific heat is given by:

$$C_X = C_P - V\frac{\frac{2\sigma}{3rT}}{1 - \frac{2\sigma}{3rP}} = C_P - V\frac{\frac{P}{T}}{\frac{3rP}{2\sigma} - 1}$$

We then have:

$$C_X = C_P - \frac{\frac{PV}{T}}{\frac{3rP}{2\sigma} - 1} = C_P - \frac{nR}{\frac{3rP}{2\sigma} - 1}$$

If we use $P = P_o + \frac{2\sigma}{r}$, we finally have:

$$C_X = C_P - \frac{nR}{\frac{3rP_o}{2\sigma} + 2}$$

Note that, when $\sigma = 0$, $C_X = C_P$.

Question 5

a) The only way to transfer heat from high temperature to low temperature is by an irreversible process:

INCORRECT

It is possible to to transfer heat *reversibly* from a high temperature thermal reservoir to a low temperature thermal reservoir. An example: The Carnot Cycle. The first three stages of this cycle are:

1. Isothermal Expansion: Heat is withdrawn from hot region to intermediate system, or working fluid, at the same temperature.

2. Adiabatic Expansion: The system decreases its temperature at constant entropy.

3. Isothermal Compression:The system is isothermally compressed while in contact with the cold reservoir. The heat taken from the hot region is transferred to the cold region in this step.

b) If the thermal expansion is negative, the constant pressure heat capacity is smaller than the constant volume heat capacity

INCORRECT

Using mathematical manipulations and Maxwell Relations, we have:

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

The difference between C_P and C_V is always positive.

c) Enthalpy is a conserved quantity

INCORRECT

An example of this is when work is converted to heat. Think of the stirring of a liquid. When a liquid is stirred, its temperature raises, increasing its enthalpy. In this case, there are no obvious sources of enthalpy.

d) In an adiabatic expansion of a material the temperature always goes down

INCORRECT

Think of the adiabatic free expansion of an ideal gas. In this case, since the energy of the system remains constant, there cannot be a change in its temperature.

In a general case, it is possible to show that:

$$\left.\frac{\partial T}{\partial V}\right)_S = \frac{-\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{-\left(\frac{\partial P}{\partial T}\right)_V}{\frac{C_V}{T}} = \frac{T\alpha}{C_V\beta_T}$$

$$dT = \frac{T\alpha}{C_V \beta_T} dV$$

Note that the change in temperature, dT depends on the sign of α, for any given change in volume, dV.

e) The entropy of a system can decrease

CORRECT

An example of this is solidification. In this case, the system reduces its entropy when it transforms to the solid phase. The environment, however, increases its entropy due to the removal of heat from the solidifying system.