

Final Exam
Solutions
3.20 MIT
Fall 2001

Problem 1

(a & b) Sources of irreversibility

- Bucket falling: potential energy is dissipated as heat in the environment at $25^\circ C$

Energy:

$$mgh = 1 * 9.8 * 2 = 19.6 J$$

Dissipated as heat into environment

$$\Delta S = \frac{19.6 J}{298 K} = 0.0658 \frac{J}{K}$$

- Water evaporating

-Calculate the entropy difference between $S(0.03 \text{ atm})$ and $S(0.01 \text{ atm})$.

-Imagine water evaporating against 0.03 atm \rightarrow this process is reversible

-Expansion from 0.03 \rightarrow 0.01 atm is irreversible

(NOTE: the irreversibility arises from the fact that the H_2O evaporates into a gas phase with $P_{H_2O} = 0.01 \text{ atm}$, where as $P_{H_2O}^{equilibrium} = 0.03 \text{ atm}$ at $25^\circ C$.)

$$\Delta S = -\frac{1kg}{18 \frac{g}{mol}} * 8.314 \frac{J}{mol - K} \ln \left(\frac{0.01}{0.03} \right)$$

$$\Delta S = 0.5074 \frac{J}{K}$$

Problem 2

(a) Elastic interactions always make a positive contribution to the enthalpy of formation. Think about it.

- Elements A and B can be by themselves in ideal geometry. When mixed, A has to adapt to the lattice parameter preferred by B and vice versa \rightarrow No one is happy \rightarrow positive enthalpy of formation.

- For a size difference of 15% the ΔH becomes too large to see miscibility.

(b)

- Size

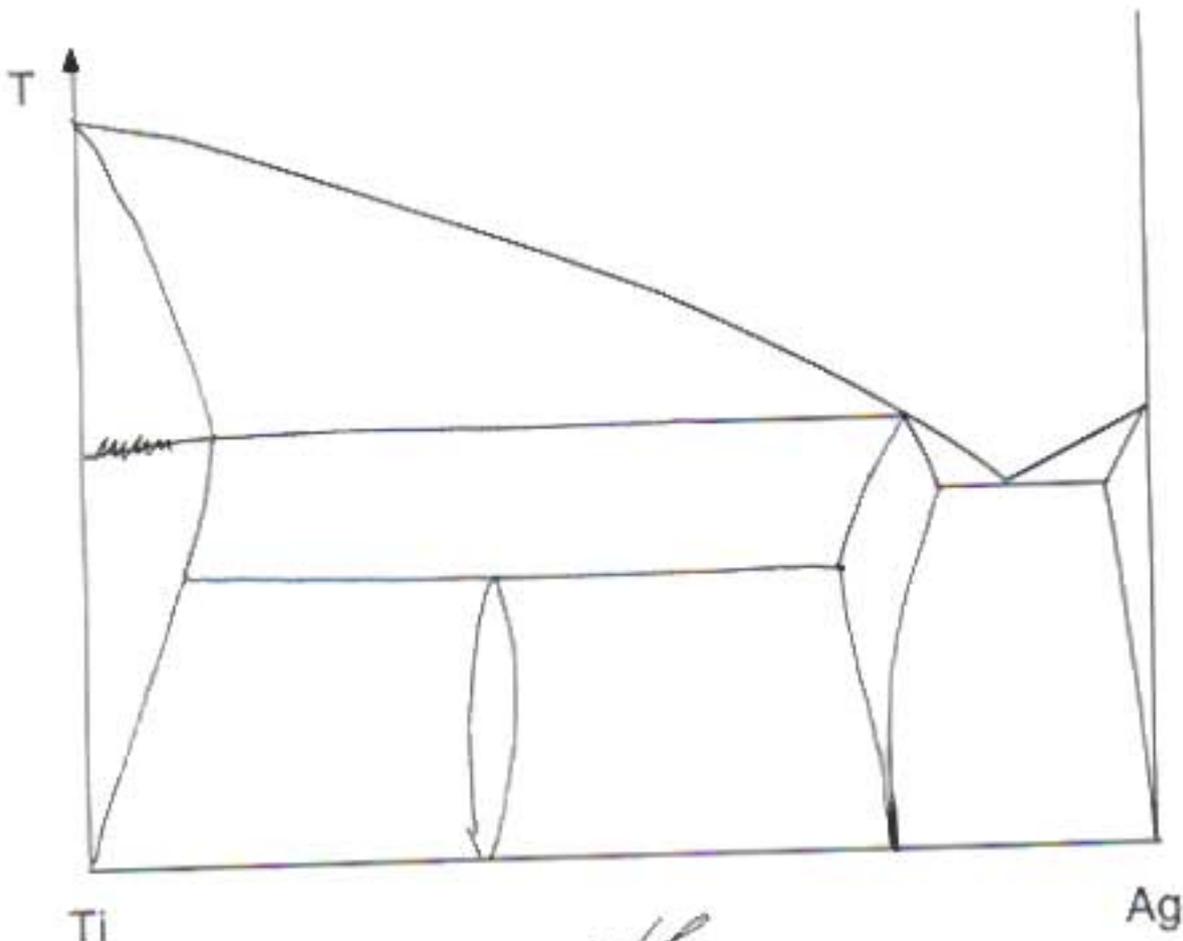
$$\frac{\Delta V}{V} \approx \frac{0.3}{10.5} \approx 3\% \implies \frac{\Delta a}{a} = \frac{1}{3} \frac{\Delta V}{V} = 1\%$$

\rightarrow there is not much elastic interactions

- Electronegativity

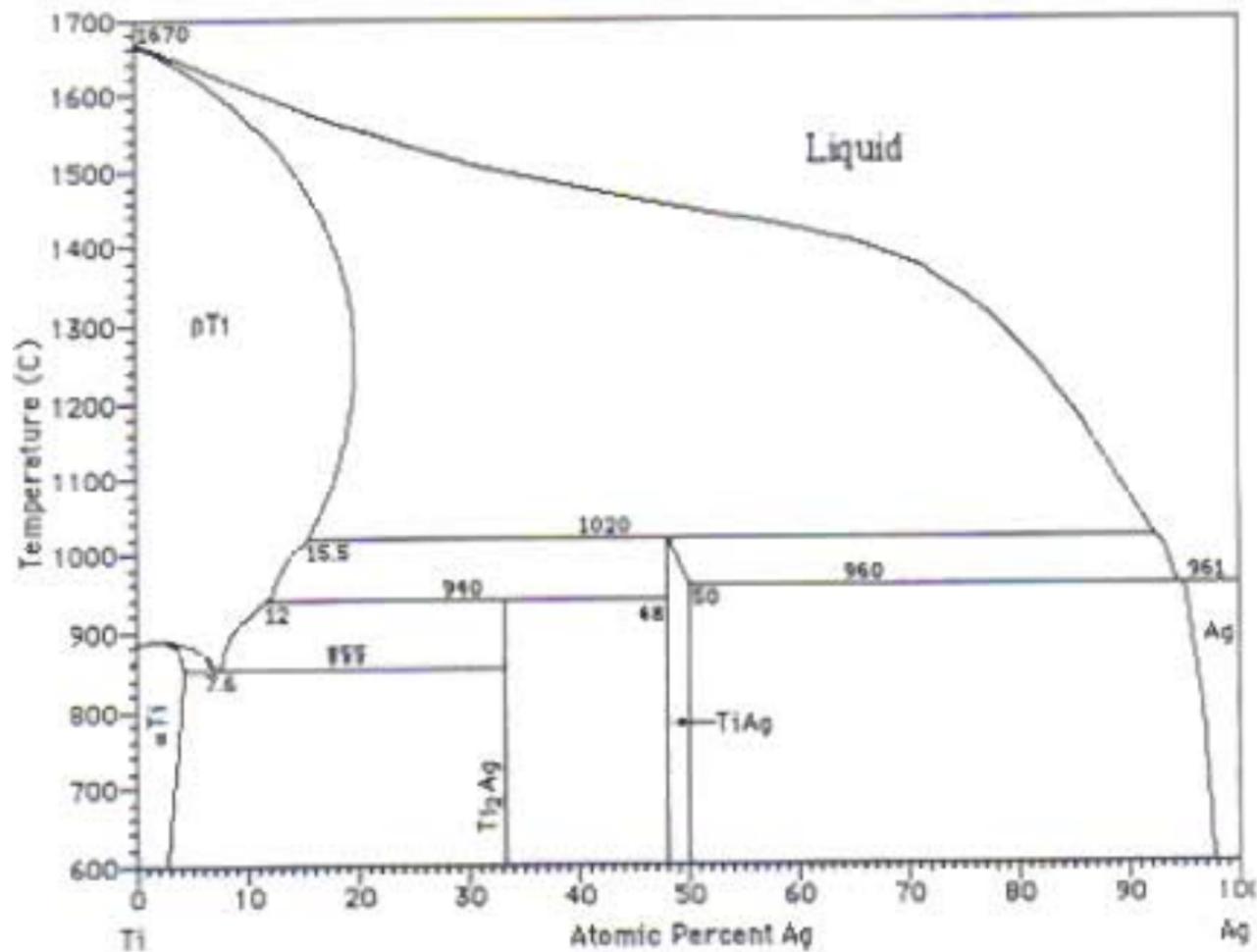
Ti and Ag are on opposite sides of the transition metal series. We expect some electronegativity difference \implies Compound forming.

(c) see next page



possible
only one^v example.

The real Ti-Ag phase diagram
is on the next page.



Problem 3

(a) It is important to remember that we are NOT talking about an ideal gas, thus $\Delta U \neq 0$. We can write the Gibbs free energy as

$$dG = -SdT + \sigma dA + \dots$$

and from this we can obtain the following Maxwell relation

$$\left(\frac{\partial \sigma}{\partial T}\right)_A = -\left(\frac{\partial S}{\partial A}\right)_T$$

Then

$$\left(\frac{\partial \sigma}{\partial T}\right)_A = \frac{C}{T} = -\left(\frac{\partial S}{\partial A}\right)_T$$

Thus

$$\boxed{\frac{\Delta S}{\Delta A} = -\frac{C}{T}}$$

(b) What is $\left(\frac{\partial T}{\partial A}\right)_S = ?$

$$\left(\frac{\partial T}{\partial A}\right)_S = -\frac{\left(\frac{\partial S}{\partial A}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_A} = -\frac{-\frac{C}{T}}{\frac{c_A}{T}} = \frac{C}{c_A} > 0$$

(Note C is the constant given in $\sigma = B + C \ln T$).

- Therefore the temperature must increase when the material is separated adiabatically ($\left(\frac{\partial T}{\partial A}\right)_S > 0$)

Problem 4

(b) This was a trick question. For a random solution:

$$P_{AA} = (P_A)^2 = x_A^2 = (0.5)^2 = 0.25$$

Hence when $P_{AA} = 0.25 \rightarrow$ solution is random \rightarrow already has maximal entropy. Changing P_{AA} in either direction will lower the entropy.

(c) No. The Second Law states that in a cyclic process the only result can not be that heat from one T is converted to work. The process described is not cyclic. The battery is losing internal energy.

(d) In a lattice model, only configurational entropy is included. The high temperature limit of S_{config} is $k_b [x \ln x + (1-x) \ln(1-x)]$ which is not dependent on T. Hence $C_{config} = T \left(\frac{\partial S_{config}}{\partial T}\right) = 0$. The Dulong and Petit limit for C actually comes from the vibrational entropy.

Problem 5

The best approach to this problem is to write everything using stress and strain. By doing this you avoid problems with sign conventions and units.

- Define elongation state with $\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}$.
 \rightarrow The conjugate variables are $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$
- In this terminology, $C_p = C_{\sigma_{xx}, \sigma_{yy}, \sigma_{zz}}$
- We are asked to relate the heat capacity at constant length ($C_l = C_{\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}}$) to c_p .
- Using the given relation we can write

$$\left(\frac{\partial S}{\partial T}\right)_{\varepsilon_{xx}} = \left(\frac{\partial S}{\partial T}\right)_{\sigma_{xx}} + \left(\frac{\partial S}{\partial \sigma_{xx}}\right)_T \left(\frac{\partial \sigma_{xx}}{\partial T}\right)_{\varepsilon_{xx}}$$

• Now we must reduce these partials do get in terms of things we know. First, we can get a Maxwell relation by writing dG as

$$dG = -SdT - \varepsilon_{xx}Vd\sigma_{xx} \dots$$

$$\left(\frac{\partial S}{\partial \sigma_{xx}} \right)_T = V \left(\frac{\partial \varepsilon_{xx}}{\partial T} \right)_{\sigma_{xx}}$$

• The other term $\left(\frac{\partial \sigma_{xx}}{\partial T} \right)_{\varepsilon_{xx}}$ can be written as

$$\left(\frac{\partial \sigma_{xx}}{\partial T} \right)_{\varepsilon_{xx}} = - \frac{\left(\frac{\partial \sigma_{xx}}{\partial \varepsilon_{xx}} \right)_T}{\left(\frac{\partial T}{\partial \varepsilon_{xx}} \right)_{\sigma_{xx}}}$$

• Putting this all together

$$\frac{C_{\varepsilon_{xx}, \sigma_{yy}, \sigma_{zz}}}{T} = \frac{C_{\sigma_{xx}, \sigma_{yy}, \sigma_{zz}}}{T} - V \underbrace{\left(\frac{\partial \sigma_{xx}}{\partial \varepsilon_{xx}} \right)_T}_E \left[\underbrace{\left(\frac{\partial \varepsilon_{xx}}{\partial T} \right)_{\sigma_{xx}}}_{\alpha_L} \right]^2$$

So,

$$C_L = C_p - TVE\alpha_L^2$$

Problem 6

(a)

$$L = NL_1 + (M - N)L_2 = L_N$$

$$E = N\varepsilon_1 + (M - N)\varepsilon_2 = E_N$$

(b) The partition function is defined as

$$\Gamma = \sum_{states} e^{-\beta(E-FL)}$$

$$\Gamma = \sum_{N=0}^M \frac{M!}{(M-N)!N!} e^{-\beta(E_N-FL_N)}$$

$$\Gamma = \sum_{N=0}^M \frac{M!}{(M-N)!N!} \left[e^{-\beta(\varepsilon_1-FL_1)} \right]^N \left[e^{-\beta(\varepsilon_0-FL_0)} \right]^{M-N}$$

$$\Gamma = \left(e^{-\beta(\varepsilon_1-FL_1)} + e^{-\beta(\varepsilon_0-FL_0)} \right)^M$$

(c) Let ϕ be the appropriate thermodynamic potential at constant T and F .

$$\phi = U - TS - FL \quad \text{and} \quad \phi = -kT \ln \Gamma$$

$$d\phi = -SdT - LdF$$

$$L = - \frac{\partial \phi}{\partial F} = \frac{-kT}{\Gamma} \frac{\partial \Gamma}{\partial F}$$

$$L = M \left\{ \frac{L_1 e^{-\beta(\varepsilon_1-FL_1)} + L_0 e^{-\beta(\varepsilon_0-FL_0)}}{e^{-\beta(\varepsilon_1-FL_1)} + e^{-\beta(\varepsilon_0-FL_0)}} \right\}$$

Problem 7

The pressures outside the cylinder were given as $P_A = 0.6$ and $P_B = 0.2$ atm. Let the pressures inside be given by P_A^i and P_B^i .

We are told that the piston is semi-permeable to B, thus:

$$P_B = P_B^i$$

The initial partial pressures:

$$P_A^i + P_B^i = 1 \text{ atm}$$

$$P_B^i = 0.2 \text{ atm}$$

$$\implies P_A^i = 1 - 0.2 = 0.8 \text{ atm}$$

(a) The volume is reduced by half

$$P_A^i = \frac{n_A RT}{V}$$

So,

$$V \rightarrow \frac{V}{2} \implies P_A^i \rightarrow 2P_A^i$$

$$P_A^i = 1.6 \text{ atm}$$

$$P_B^i = 0.2 \text{ atm}$$

since B is still in equilibrium with the environment..

(b)

$$P_{tot} = P_A^i + P_B^i + P_C^i = 1.6 + 0.2 + 0.15 = 1.95 \text{ atm}$$

(c)

$$P_A^i = 1.6$$

$$P_B^i = 0.2$$

$$P_{BC}^i = 0.15$$

$$P_C^i = 0$$

$$P_{tot} = P_A^i + P_B^i + P_C^i + P_{BC}^i = 1.95 \text{ atm}$$