Question 1:   (Ceoler)

A turbine is extracting mechanical work from steam at high pressure in a steady state process. The temperature of the steam is 400°C at the inlet and its pressure is 20 atm. At the outlet the temperature is 200°C and the pressure 1.5atm. The rate of steam through the turbine is 300 moles/second. The turbine itself operates adiabatically.

a) What is the rate of the entropy change of the turbine ?
b) What is the entropy change of the steam per mole going through the turbine ?
c) What is the rate of entropy change for the universe ? Only consider the process as described. Do not consider how the steam might be generated.

DATA: Heat capacity of steam can be approximated to 37 J/mol-K in this temperature range.

a) $\Delta S_{turbine} = 0$ since turbine does not change

b) $S(T,p) \Rightarrow ds = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

$$\hookrightarrow = C_p/T \qquad \hookrightarrow = \left(\frac{\partial V}{\partial T}\right)_p = -\frac{R}{p} \quad (\text{for } IG)$$

$$ds = C_p \frac{dT}{T} - R \frac{dp}{p}$$

$$\Delta S = C_p \ln T_2/T_1 - R \ln P_2/P_1$$

$$= 37 \frac{J}{mol\text{-}k} \ln \frac{473}{673} - 8.314 \ln \frac{1.5}{20} = \boxed{8.49 \; J/mol\text{-}k}$$

c)   Only steam undergoes entropy change.

Hence $\Delta \dot{S}_{universe}$ = 300 moles/sec × 8.49 J/mol-k

$$= \boxed{2.548 \; kJ/K\text{-}s}$$

Question 2: (Paul)

a) What can you say about the sols, A and B, from the following information concerning the relative molar critical coagulation concentrations (CCCs)? CCC's (Relative concentrations)

Electrolyte	Sol A	Sol B
KCl	64	64
$MgCl_2$	32	1
Na_2SO_4	1	32

b) Draw curves that depict the potential energy of interaction $V(h)$ between two colloidal particles as a function of their separation h for the following conditions (express relevant energies in units of kT):

(1) a stabilized sol that experiences slow coagulation; and
(2) a sol that experiences rapid coagulation.
(3) How do you convert a sol from condition (1) to condition (2)?

ⓐ Sol A: CCC is linear with anion concentration
and vanishes as $1/z^6$ with anion ~~concentration~~ valence/.
⇒ ● Sol A is positively charged

Sol B: CCC is linear with cation concentration
and vanishes as $1/z^6$ with cation valence.
⇒ Sol B is negatively charged sol.

ⓑ (1)

(2)
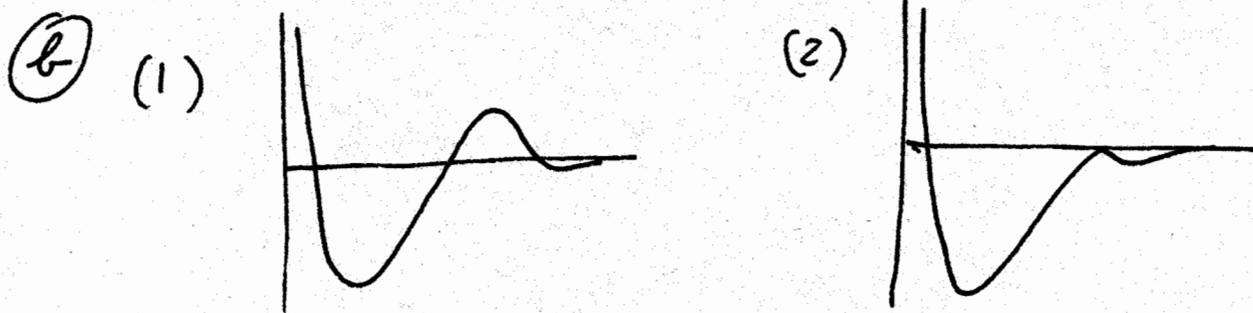
(3) Add more salt, increase valence of salt by adding higher valence salt.

Question 3   (Pav l)

For n-octane, the surface tension is 21.8 mJ/m2, and the interfacial
tension on water is 50.8 mJ/m2. Comment on the long-term spreading behavior
of this hydrocarbon on water. (The surface tension of water is 72.8 mJ/m2.)

$$S = \sigma_{wv} - \left(\sigma_{octane-vapor} + \sigma_{octane-water} \right)$$
$$= 72.8 - (21.8 + 50.8) = 0.2 \; mJ/m^2$$

The oil initially spreads on the water
but after some contamination of the water
by n-octane, σ_{wv} will decrease and S becomes
negative, so it reverses to form surface
lens almost immediately

Problem 4 (Cedar)

The heat capacity C_X is related to the temperature derivative of the entropy under the condition X.

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dp$$

/ dT
and take
constant X

$$\left(\frac{ds}{dT}\right)_X = \frac{C_p}{T} + \left(\frac{\partial s}{\partial P}\right)_T \left(\frac{\partial p}{\partial T}\right)_X$$

$$\longrightarrow \; = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha_v V$$

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

Since $V - ap = $ constant $\Rightarrow dV = \alpha\, dp$

$$\left(\frac{\partial p}{\partial T}\right)_X = \frac{1}{\alpha}\left(\frac{\partial V}{\partial T}\right)_X \longrightarrow$$

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

$$\underset{-\alpha_v V}{\Vert} \qquad \underset{-\beta_T V}{\Vert}$$

$$\left(\frac{dV}{dT}\right)_X = -\alpha_v V - \beta_T V\left(\frac{\partial p}{\partial T}\right)_X$$

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

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_X = \frac{-\alpha_v V \alpha}{\alpha + \beta_T V}$$

$$\boxed{C_X = C_p - \frac{T(\alpha_v V)^2}{\alpha + \beta_T V}}$$

$T\left(\frac{\partial s}{\partial t}\right)_X$

Question 5:

a) Sketch the heat capacity C_v as function of temperature for an elemental solid in the Einstein model. Please label the axis. Pay attention to limiting values and mark them on your graph in units of R (the gas constant).

b) Discuss clearly the *mechanism* that makes the heat capacity go to zero as the temperature goes to zero. No equations necessary.

c) If I were to model the same system with a *classical* molecular dynamics simulation and plot the heat capacity from the simulation (e.g calculated as the derivative of the energy with temperature)) as a function of temperature what would it look like ? Make a *plot* again marking all the limiting values. *Explain.* Think carefully of why the heat capacity goes to zero in part a).
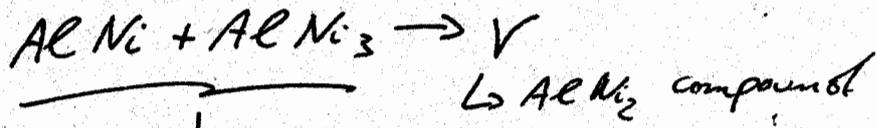
a)
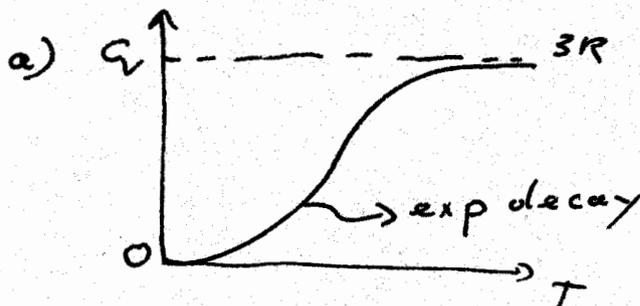
b) Heat capacity goes to zero because of discreetness of states (quantization). This implies that below a certain temperature, there is simply not enough thermal energy to cross the gap between occupied and unoccupied states. This is <u>not</u> the case when a continuum of states exists

c)
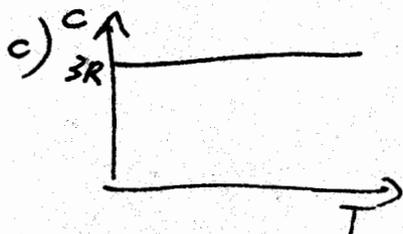
In classical statistical mechanics there is <u>always</u> enough thermal energy for excitations as there is always an unoccupied state infinitesimally close to the occupied states
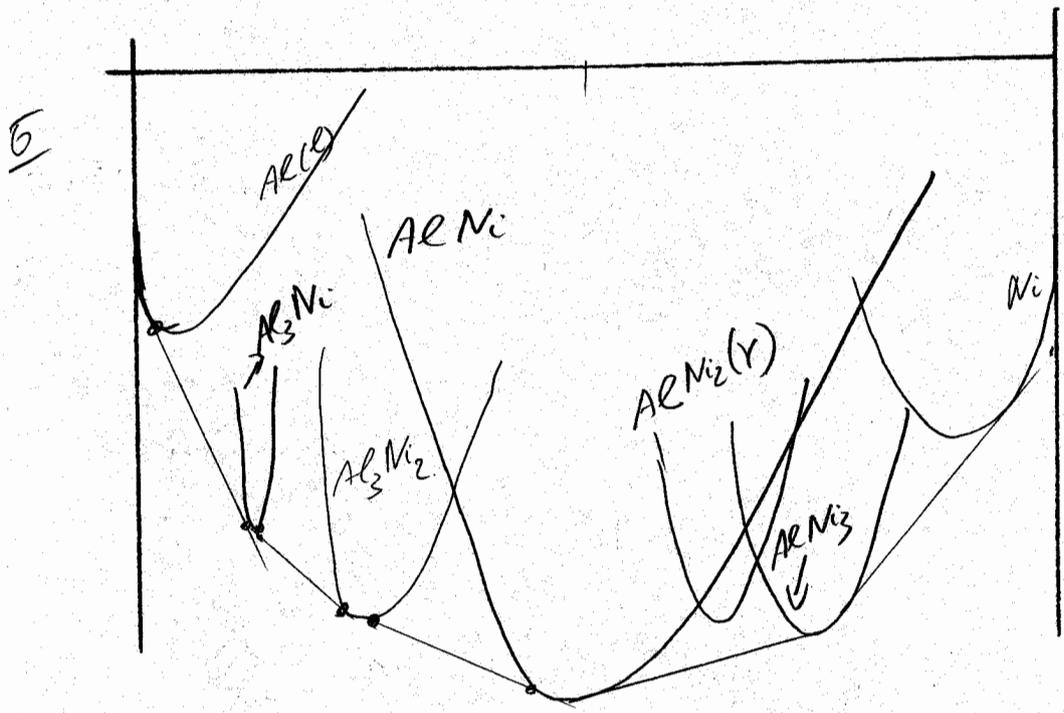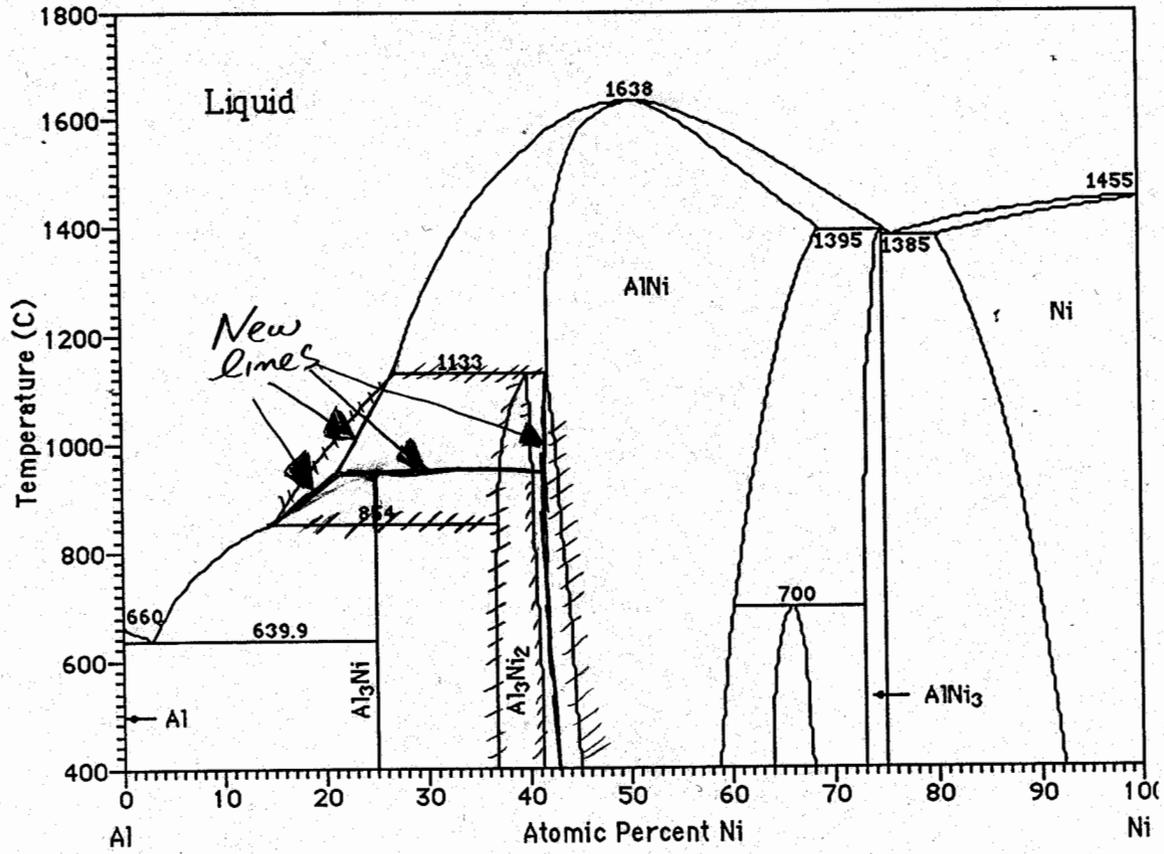
Question 6 continued

b) at 700°C peritectoid reaction.

$$AlNi + AlNi_3 \rightarrow \gamma$$

$$\underbrace{}_{}$$
↓
These two solids
have to react together
to form γ

└→ $AlNi_2$ compound

c)

σ

Al(s)

AlNi

Al₃Ni

Al₃Ni₂

AlNi₂(γ)

AlNi₃

Ni

Al–Ni phase diagram

Problem 7

Consider the capacitor below. It is characterized by the following extensive variables: thickness of the dielectric l, charge on the capacitor q and entropy S. The conjugate variables are force f, electrical potential ϕ, and temperature T. The characteristic function U is a function of U(S, l, q).

a) In many practical cases it is easier to control T and f. Define the *Legendre transform* B(T, f, q) that gives me a thermodynamic potential with natural variables T, f and q, and write its *differential*.

b) The properties of this system are defined by all the possible second derivatives of this Legendre transform. How many different properties are there ? Write the matrix of second derivatives of B in terms of the following properties.
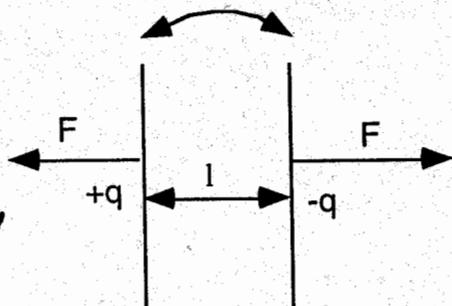
C: Heat capacity
α Linear thermal expansion
Cap: capacitance (Use "Cap" to distinguish from heat capacity)
d: piezoelectric coefficient (measure of potential change with force)
p: pyroelectric coefficient (measure of potential change with temperature)
A: elastic compliance

$$dU = Tds + fdl + \phi dq$$

$$B = U - TS - fl$$

$$dB = -sdT - ldf + \phi dq \Rightarrow B(T, f, q)$$

$$\frac{\partial^2 B}{\partial T^2} = -\left(\frac{\partial s}{\partial T}\right)_{f,q} = -\frac{C_{f,q}}{T}$$

$$\frac{\partial^2 B}{\partial T \partial f} = -\frac{\partial l}{\partial T} = -l\alpha_L = \frac{\partial^2 B}{\partial f \partial T}$$

$$\frac{\partial^2 B}{\partial T \partial q} = \frac{\partial \phi}{\partial T} = p = \frac{\partial^2 B}{\partial q \partial T}$$

$$\frac{\partial^2 B}{\partial f^2} = -\frac{\partial l}{\partial f} = -lA$$

$$\frac{\partial^2 B}{\partial f \partial q} = \frac{\partial \phi}{\partial f} = d = \frac{\partial^2 B}{\partial q \partial f}$$

$$\frac{\partial^2 B}{\partial q^2} = \frac{\partial \phi}{\partial q} = \frac{1}{cap}$$

	T	f	q
T	$-\dfrac{C_{f,q}}{T}$	$-l\alpha_L$	p
f	$-l\alpha_L$	$-lA$	d
q	p	d	$\dfrac{1}{cap}$

Problem 8

a) Assuming that Ga and As form an ideal solution in the liquid phase, estimate the melting temperature of the compound GaAs. The GaAs compound may be considered to be a line-compound (i.e. it allows no off-stoichiometry or disorder).

b) The real transition temperature is 1,511K. Explain why the temperature you find is higher.

DATA:

The formation energy of GaAs (s) from solid Ga and As is:

$\Delta G_f = -74,100 - 12.5T$ (in J/mole, T in Kelvin)

For pure Ga:
T_m is 303 K
$\Delta G_m = 6620 - 21.85\,T$ (in J/mole, T in Kelvin)

For pure As:
T_m is 1090 K
$\Delta G_m = 5604 - 5.14\,T$ (in J/mole, T in Kelvin)

Take reference state solid Ga and As

Liquid: $G_\ell = \Delta G_m^{Ga} + \Delta G_m^{As} + 2RT\left[\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right]$

Solid: $G_s = \Delta G_f$

$6620 + 5604 - (21.85 + 5.14)T - 2RT\ln 2 = -74,100 - 12.5T$

$86,324 = \dfrac{(21.85 + 5.14 + 11.52 - 12.5)T}{26.01}$

$\boxed{T = 3,318K}$