3.20 Fall 2002 Exam 2 Solutions

a) USE PRESCRIPTION GIVEN IN CLASS (OR ANY OTHER METHOD THAT WORKS FOR YOU).

$$dU = TdS + f d\ell = d\bar{E}$$

$$U = TS + f\ell = \bar{E} \quad \text{(Euler)}$$

$$\frac{S}{k} = \beta\bar{E} - \beta f \ell \qquad S(\bar{E}, \ell)$$

WE ARE WORKING AT CONSTANT T, f, SO NEED TO PERFORM LEGENDRE TRANSFORM

$$\underbrace{\frac{S}{k} - \beta\bar{E} + \beta f \ell}_{\sum_\eta e^{\square}} = -\beta\phi$$

$$\boxed{\Lambda = \sum_\eta e^{-\beta(E_\eta - f\ell_\eta)}}$$

THE SUM OVER STATES INCLUDES A SUM OVER ALL ALLOWED LENGTHS

b) $$\bar{\ell} = \frac{\sum_\eta \ell_\eta e^{-\beta(E_\eta - f\ell_\eta)}}{\Lambda}$$

* $$\bar{\ell}\Lambda = \sum_\eta \ell_\eta e^{-\beta(E_\eta - f\ell_\eta)}$$

* conjugate to ℓ is f $\rightarrow$ take derivative w.r.t. f

l.h.s. $$\frac{\partial(\bar{\ell}\Lambda)}{\partial f} = \Lambda\frac{\partial\bar{\ell}}{\partial f} + \bar{\ell}\frac{\partial\Lambda}{\partial f} = \Lambda\frac{\partial\bar{\ell}}{\partial f} + \bar{\ell}\sum_\eta \beta\ell_\eta e^{-\beta(E_\eta - f\ell_\eta)}$$

r.h.s $\frac{\partial}{\partial f}\left(\sum_{\eta} l_\eta e^{-\beta(E_\eta - f l_\eta)}\right) = \beta \sum_{\eta} l_\eta^2 e^{-\beta(E_\eta - f l_\eta)}$

divide both sides by Λ

$$\frac{\partial \bar{l}}{\partial f} + \bar{l}\ \underbrace{\frac{\sum_\eta \beta l_\eta e^{-\beta(E_\eta - f l_\eta)}}{\Lambda}}_{\beta \bar{l}} = \beta\ \underbrace{\frac{\sum_\eta l_\eta^2 e^{-\beta(E_\eta - f l_\eta)}}{\Lambda}}_{\overline{l^2}}$$

$$\frac{\partial \bar{l}}{\partial f} + \beta \bar{l}^2 = \beta \overline{l^2}$$

or $\overline{l^2} - \bar{l}^2 = kT \frac{\partial \bar{l}}{\partial f}$

we also know that

$$\frac{\partial \bar{l}}{\partial f} = \alpha$$

$$\Rightarrow \boxed{\overline{l^2} - \bar{l}^2 = kT\alpha}$$

(constant (E, N, V))

(2) a) For an isolated system, the second law states that a spontaneous process will occur if the final state has a larger entropy than the initial state,

$\Delta S = S_f - S_i > 0.$

From stat-mech we know that $S = k \ln \Omega$ where Ω is the degeneracy at the fixed energy E of the system. This means that

$$\Delta S = S_f - S_i = k \ln \Omega_f - k \ln \Omega_i = k \ln\left(\frac{\Omega_f}{\Omega_i}\right) > 0$$

or $\Omega_f > \Omega_i$. Hence for a spontaneous process, the system evolves to the state with maximal degeneracy (maximal number of micro states). This can occur if some internal restraint in the system is removed (e.g. add a catalyst).

b) The third law states that the entropy of a system goes to zero as $T \to 0$.

From stat-mech we know that

$$P_\nu = \frac{1}{\Omega_0} \quad \text{if } \nu \text{ is a ground state}$$ (Ω_0 = degeneracy of lowest energy state)

$$P_\nu = 0 \quad \text{if } \nu \text{ is not a ground state}$$

$$S = \sum_\nu P_\nu \ln P_\nu = k \ln \Omega_0$$

2 b) continued.

Ω_0 for the groundstate is typically ~~≈~~ 1 or 2, and ~~[illegible]~~ rarely exceeds $N \sim 10^{23}$

Hence $S \approx k \ln 10^{23} \sim 23\,k$ (= small)

$$\Rightarrow \quad \frac{S}{N} \sim \frac{23\,k}{10^{23}} \to 0$$

a) * adsorbed atoms are independent & distinguishable

* single particle energies are $\varepsilon_n = (n+\tfrac{1}{2})h\nu$

$$\Rightarrow \quad Q = q^M \qquad q = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_n}$$

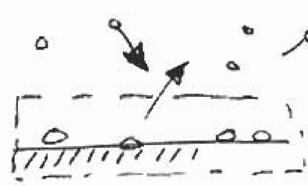
$$q = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})h\nu} = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}$$

b) $N < M \Rightarrow$ this results in configurational disorder with degeneracy

$$\Omega = \frac{M!}{N!(M-N)!}$$

$$Q = \Omega q^N = \frac{M!}{N!(M-N)!} q^N$$

c) $\bar{N} = ?$ when surface is in equilibrium with gas of arsenic at constant μ.



Grand canonical ensemble

$$\Theta = \sum_{N=0}^{M} Q(N,V,T)\, e^{\beta\mu N}$$

$$= \sum_{N=0}^{M} \frac{M!}{N!(M-N)!} q^N e^{\beta\mu N} = \underbrace{\sum_{N=0}^{M} \frac{M!}{N!(M-N)!} (q e^{\beta\mu})^N (1)^{M-N}}_{\text{Binomial expansion}}$$

$$\boxed{\Theta = (1 + q e^{\beta\mu})^M}$$

3 C CONTINUED

In the grand canonical ensemble

$$\bar{N} = +\frac{kT\,\partial \ln \Theta}{\partial \mu} = +\,kT\,M\,\frac{\partial \ln\left(1+qe^{\beta\mu}\right)}{\partial \mu}$$

$$= +kT\,M\left(\frac{\beta\, q e^{\beta\mu}}{1+qe^{\beta\mu}}\right) = \frac{M\, q e^{\beta\mu}}{\left(1+q e^{\beta\mu}\right)}$$

Alternative way of solving 3c). Use equivalence of ensembles; and work in canonical ensemble

$$\Rightarrow \mu = -kT\frac{\partial \ln Q}{\partial N} \quad \text{with} \quad Q = \frac{M!}{N!(M-N)!}\,q^N$$

$\Downarrow$

use stirling

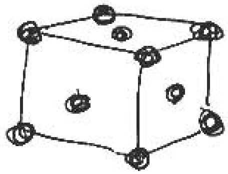
⋮

4) Partial molar volume of Ti

$$\bar{V}_{Ti} = \frac{\partial (N\underline{V})}{\partial N_{Ti}} = \underline{V} + \frac{\partial \underline{V}}{\partial x}(1-x) \qquad x = \frac{N_{Ti}}{N_{Ti}+N_{Al}}$$

see notes in class (intercept rule)

$$\underline{V} = \frac{a^3}{4}$$



fcc has four atoms per cubic unit cell

$$\frac{\partial \underline{V}}{\partial x} = \frac{3a^2}{4}\frac{da}{dx}$$

$$\bar{V}_{Ti} = \frac{a^3}{4} + \frac{3a^2}{4}\frac{da}{dx}(1-x)$$

$$a(x=0.25) \approx 3.3$$

$$\frac{da(x=0.25)}{dx} \approx \frac{2.4-3.7}{1-0} = -1.3$$

substitute into

5)

a) $$\Omega = \left(\frac{N!}{n!(N-n)!} \right)^2$$

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

(since vacancies & interstitials don't interact energetically, every configuration has the same energy)

$$S = 2k \ln \left(\frac{N!}{n!(N-n)!} \right)$$

$$= 2k \left\{ N \ln N - \cancel{N} - n \ln n + \cancel{n} - (N-n) \ln (N-n) + \cancel{(N-n)} \right\}$$

$$= 2k \left\{ N \ln \left(\frac{N}{N-n} \right) + n \ln \left(\frac{N-n}{n} \right) \right.$$

$$= 2kN \left\{ \ln \left(\frac{1}{1-x} \right) + x \ln \left(\frac{1-x}{x} \right) \right.$$

$$S = -2kN \left\{ (1-x) \ln (1-x) + x \ln x \right\}$$

c) entropy will go down, because entropy of part b) is already maximal. Any time certain microstates are energetically favored, i.e. have higher probability of occurring, the entropy will be lower than when all microstates have equal probability of occurring.