5.62 Physical Chemistry II
Spring 2008

<u>Information for Hour Exam</u>

The exam will be closed book and closed notes, but you will be allowed one sheet of 8.5 × 11" paper (both sides) with your own notes, equations, and inspirational quotations.

**YOU MUST BRING A "SIMPLE" CALCULATOR!!**

MATERIAL COVERED:

Lectures 1-12
Problem Sets 1-3

Combinatorics

All thermodynamic quantities (U, H, A, G, S, $\mu$, $C_V$, $C_p$, p) from Q.

Multinomial trick and, for $\bar{n}_i \ll 1$, replace $\dfrac{N!}{\prod_i n_i!}$ by N!

$Q = \dfrac{q^N}{N!}$ provided that q ≫ N, equivalent to $e^{-\mu/kT} = q/N \gg 1$

$$\bar{n}_i = \frac{1}{e^{(\varepsilon_i - \mu)/kT} \pm 1} \qquad \text{(+1 FD, no 1 B, –1 BE)}$$

ω(n,g) for BE, B, and FD

$$\bar{n}_i^{FD} \le \bar{n}_i^{B} \le \bar{n}_i^{BE}$$

$$\varepsilon_{L,M,N} = \frac{h^2}{8m}\left[\frac{L^2}{a^2} + \frac{M^2}{b^2} + \frac{N^2}{c^2}\right]$$

$$q_{trans} = \left[\frac{2\pi mkT}{h^2}\right]^{3/2} V \qquad V = abc$$

(crucial approximation in deriving $q_{trans}$?)

$\varepsilon \to q \to Q \to$ thermodynamic quantities. Key is ln(q) permits all key contributions to be separated as additive factors.

**Classical Mechanical formulation**

$$q_{Cl} = h^{-3} \int \cdots \int d\underset{\sim}{q}^3 d\underset{\sim}{p}^3 e^{-\varepsilon(\underset{\sim}{q}^3, \underset{\sim}{p}^3)/kT}$$

Equipartition: $\varepsilon = (1/2)kT$ per $p^2$ or $q^2$ degree of freedom [H(**p**,**q**)] per particle.

Probability distributions.
Change of variable.
Density of states.
Dimensional analysis.

$$P(\varepsilon_x)d\varepsilon_x = P(L)dL$$

$$P(\varepsilon_x) = \underbrace{\frac{dL}{d\varepsilon_x}}_{\text{densit states}} P(L) \qquad \left(\text{want } \frac{dL}{d\varepsilon_x} \text{ and } P(L) \text{ as explicit functions of } \varepsilon_x\right)$$

$$P(\varepsilon_x) = (\pi kT)^{-1/2} \varepsilon_x^{-1/2} e^{-\varepsilon_x/kT}$$

verify by normalization

verify by computing $\bar{\varepsilon}$ and finding agreement with $\bar{\varepsilon} = kT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$

$$\bar{x} = \int_0^\infty P(x(\varepsilon))x(\varepsilon)e^{-\varepsilon/kT}d\varepsilon$$

$$q(T, \ \ ) = q_{trans} q_{int}$$

$$Q(N, T, \ \ ) = \left(\frac{q_{trans}^N}{N!}\right) q_{int}^N$$

Internal degrees of freedom: electronic, vibration, rotation, nuclear spin.

Low T limit.
High T limit.

$q_{elect} = g(\varepsilon_0)$ lowest electronic state.

For diatonics: $\begin{cases} q_{rot} = \dfrac{kT}{\sigma hcB_e} + \dfrac{1}{2} + \ldots \\ B_e = \dfrac{h}{8\pi^2 Ic}, I = \mu R_e^2 \end{cases}$

$\sigma$ is symmetry number.