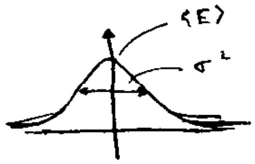
PRINT NEATLY *** **USE A BLACK PEN** *** **DO NOT STAPLE**

Course 565/665 Lecture Number ______ Date 4/3/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Last Time

Heat Capacity is proportional to the Energy fluctuations in a system: $\sigma^2 = kT_0^2 \cdot C_v$



By Friday 4/11

- Send an email:

  cavagnero@chem.wisc.edu

  with oral presentation:

  [- Title
  - 1-3 reference citation]

Change in Schedule:

~~No Class on Thursday, May 1st.~~

- 5 Classes w/ 20 minutes × 3 orals presentation
- Class will be 9:45am - 10:45am
  5/2, 5/5, 5/6, 5/8, 5/9
- Short Class on May 1st: 9:55 - 10:15 (MZ presents).

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Lecturer [redacted] Cavagnero Note Taker Fulmer

<u>Chemical Equilibria</u>

- Settle, for this chapter, on T, p constant
- Study systems towards or at equilibrium in chemical or biological transformations
- Consider ideal gases (independent particles, indistinguishable particles, no intermolecular interactions).

$$A \underset{}{\overset{K_{AB}}{\rightleftharpoons}} B \qquad K_{AB} = \frac{[B]}{[A]}.$$

don't use $\cancel{\rightarrow}$ $\cancel{\leftrightarrow}$ these to describe equilibrium

Note that equilibrium is a dynamic state. A is always going to B, and vice versa. But, at equilibrium, the rate at which A goes to B is equal and opposite to the rate in which B goes to A. Thus, on a macroscopic level, concentrations of species are constant.

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Criteria for equilibrium:

$dG = 0$ at constant T, P

$$dG = 0 = -S\cancel{dT}^{\,0} + V\cancel{dp}^{\,0} + \mu_A dN_A + \mu_B dN_B$$

At this constraint

$N_A + N_B = N$ (constant)

$dN_A + dN_B = 0$

$dN_A = -dN_B$

$$0 = \mu_A dN_A - \mu_B dN_A$$

$\boxed{\mu_A = \mu_B}$ at equilibrium.

The chemical potentials of A and B are equal.

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Can we predict equilibrium from knowledge of Q (can be sometimes inferred by simplified microscopic models)

$$q' = \sum_{j=0}^{t} e^{-\varepsilon_j/kT} = e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + \dots + e^{-\varepsilon_t/kT}$$

If we factor out $e^{+\varepsilon_0/kT}$

$$q = 1 + e^{-(\varepsilon_1 - \varepsilon_0)/kT} + e^{-(\varepsilon_2 - \varepsilon_0)/kT} + \dots \quad (1)$$

Little Digression:

For an ideal gas, $\mu = -kT \ln \frac{q}{N}$

Proof: $Q = \frac{q^N}{N!}$

$$G = -kT \ln Q = -kT \ln \frac{q^N}{N!} = -kT\left[\ln q^N - \ln N!\right]$$

Enter Stirling's Approximation $N! \simeq \left(\frac{N}{e}\right)^N$

$$= -kT\left[\ln q^N - \ln\left(\frac{N}{e}\right)^N\right] = -kT \ln \left(\frac{qe}{N}\right)^N$$

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Recall: $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$

$$\mu = \frac{\partial}{\partial N}\left(kTN \ln\left(\frac{N}{qe}\right)\right)_{P,T}$$

$$= kT \ln\left(\frac{N}{qe}\right) + kT\left(\frac{\cancel{N}\cancel{qe}}{\cancel{N}} \cdot \frac{1}{\cancel{qe}}\right)$$

$$= kT\left[\ln\frac{N}{q} - \ln e + 1\right]$$

$$= kT \ln\frac{N}{q}$$

Finally, $\boxed{\mu = -kT \ln\frac{q}{N}}$ for ideal gases

Going back to equilibrium

$$\mu_A = -kT \ln\frac{q_A'}{N_A} \qquad \mu_B = -kT \ln\frac{q_B'}{N_A}$$

Since $\mu_A = \mu_B$ at equilibrium,

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$$\frac{q_B'}{N_B} = \frac{q_A'}{N_A}$$

- at equilibrium
- ideal gases
- T, P constant

$$K_{AB} = \frac{[B]}{[A]} = \frac{N_B}{N_A} = \frac{q_B'}{q_A'}$$

$$= \frac{q_B}{q_A} e^{-(\varepsilon_{0B} - \varepsilon_{0A})/kT}$$

Let's generalize $aA + bB \overset{K_{ABC}}{\rightleftharpoons} cC$

$$K_{ABC} = \frac{q_C^{\,c}}{q_B^{\,b}\, q_A^{\,a}} \cdot e^{-(c\varepsilon_{0C} - a\varepsilon_{0A} - b\varepsilon_{0B})/kT}$$