Miscellaneous Notes

- The end is near – don't get behind.

- **All Excuses must be taken to 233 Loomis before noon, Thur, Apr. 25.**

- The PHYS 213 final exam times are
  * 8-10 AM, Monday, May 6

  * 1:30-3:30 PM, Wed, May 8

  The deadline for changing your final exam time is 10 pm, Tuesday, April 30

- Homework 6 is due <u>Tuesday</u>, Apr. 30 at 8 am. (NO late turn-in).

- Course Survey = 2 bonus points (accessible in SmartPhysics, but not until Apr. 24)

Lecture 19:

Chemical Equilibria, Surfaces, and Phase Transitions

- Chemical equilibria - Law of mass action

- Surface chemistry

Reading for this Lecture:
Elements Ch 13

Chemical Equilibrium

"Chemical" is a bit of a misnomer. We're describing any process in which things combine (or rearrange) to form new things.

These problems involve reactions like*: $aA + bB \leftrightarrow cC$, where A, B, and C are the particle types and a, b, and c are integers.

In equilibrium the total free energy, F, is a minimum.
We must have $\Delta F = 0$ when the reaction is in equilibrium,
for any reaction that takes us away from equilibrium:

$$\frac{dF}{dN_A} = \frac{\partial F}{\partial N_A} + \frac{\partial F}{\partial N_B}\frac{dN_B}{dN_A} + \frac{\partial F}{\partial N_C}\frac{dN_C}{dN_A}$$

$$= \frac{\partial F}{\partial N_A} + \frac{b}{a}\frac{\partial F}{\partial N_B} - \frac{c}{a}\frac{\partial F}{\partial N_C} \qquad \text{using } \frac{dN_A}{a} = \frac{dN_B}{b} = -\frac{dN_C}{c}$$

$$= 0$$

Therefore: $\boxed{a\mu_A + b\mu_B = c\mu_C}$

*Obviously we can have more or fewer species.

Chemical Equilibrium (2)

Treating the components as ideal gases or solutes:

$$\mu_i = kT \ln \frac{n_i}{n_{Q_i}} - \Delta_i \quad \longleftarrow \begin{array}{l}\text{Internal energy}\\\text{per molecule}\end{array}$$

Plug these chemical potentials into the equilibrium condition,
$a\mu_A + b\mu_B = c\mu_C$, and solve for the density ratios:

$$\frac{n_C^c}{n_A^a n_B^b} = K(T), \text{ where } K(T) = \frac{n_{Q_C}^c}{n_{Q_A}^a n_{Q_C}^b} e^{+\Delta/kT} \qquad \Delta \equiv c\Delta_C - a\Delta_A - b\Delta_B$$

K(T) is called the "equilibrium constant".
It depends on Δ's and T, but not on densities.
This equilibrium condition is a more general version of the law of mass action
that you saw before for electrons and holes.

The exact form of the equilibrium condition (how many things in the numerator
and denominator, and the exponents) depends on the reaction formula:

$$aA + bB \leftrightarrow cC$$

RHS $\rightarrow$ numerator
LHS $\rightarrow$ denominator
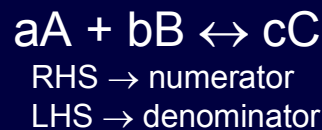
Examples of Chemical Equilibrium

Process	Reaction	Equilibrium condition
Dissociation of H_2 molecules	$H_2 \leftrightarrow 2H$	$\mu_{H2} = 2\mu_H$
Ionization of H atoms	$H \leftrightarrow e + p$	$\mu_H = \mu_e + \mu_p$
Synthesize ammonia	$N_2 + 3H_2 \leftrightarrow 2NH_3$	$\mu_{N2} + 3\mu_{H2} = \mu_{NH3}$
General reaction	$aA + bB \dots \leftrightarrow cC + dD \dots$	$a\mu_A + b\mu_B \dots = c\mu_C + d\mu_D \dots$

For the monatomic gases (circled) you can use $n_T = n_Q$.
The others are more complicated, and we won't deal with it here.
However, remember that n_T often cancels, so it won't be a problem.

Ideal solutions follow the same general form, but μ isn't close to the ideal monatomic gas value, because interactions in a liquid can be strong, modifying both U and S.

Units and notation: Chemists measure density using units of moles per liter, and write the law of mass action like this:

$$\frac{[C]^c}{[A]^a[B]^b} = K(T)$$

Chemical Equilibrium (3)

Interactions between the particles (*e.g.*, molecules):
In addition to simple PE terms from external fields, there are usually PE terms from interactions between particles (which are not usually ideal gases). Interactions between the molecules can often be neglected. That is, we'll treat the molecules as ideal gases.

Internal energy of each particle (*e.g.*, molecule):
Atoms can combine in any of several molecular forms, each of which has a different binding energy. The U term in F includes all those binding energies (which we'll call Δ's) , so they must be included in the μ's. (dF/dN)

The reaction will NOT proceed to completion in either direction, because μ depends on n for each type of molecule. As any one type becomes rare, its μ drops until equilibrium is reached, with some of each type present. (Just as not all air molecules settle into the lower atmosphere.)

ACT 1:
Equilibrium in the Ammonia Reaction

Consider a reaction that is essential to agriculture: the synthesis of ammonia from nitrogen and hydrogen:

$N_2 + 3H_2 \leftrightarrow 2NH_3$
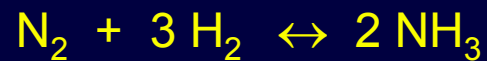
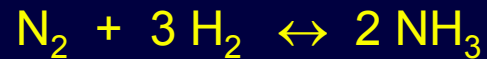1) Insert the correct superscripts and subscripts in the equilibrium equation:

$$\frac{n_{(\ )}^{(\ )} n_{(\ )}^{(\ )}}{n_{(\ )}^{(\ )} n_{(\ )}^{(\ )}} = K(T)$$

2) Suppose the reaction is in equilibrium. Now double the number of N_2 molecules. What will happen?

A) Make more NH_3.   B) Dissociate more NH_3.   C) Nothing.

Solution

Consider a reaction that is essential to agriculture: the synthesis of ammonia from nitrogen and hydrogen:

$$N_2 + 3 H_2 \leftrightarrow 2 NH_3$$

1) Insert the correct superscripts and subscripts in the equilibrium equation:

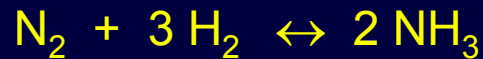$$\frac{n_{(NH_3)}^{(2)} n_{(X)}^{(\ )}}{n_{(N_2)}^{(1)} n_{(H_2)}^{(3)}} = K(T)$$

Of course, you could write the whole thing upside down, with K'(T) = 1/K(T).

2) Suppose the reaction is in equilibrium. Now double the number of N_2 molecules. What will happen?

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You've decreased the density ratio. To restore it, n_{NH3} must increase and/or n_{H2} must decrease. <u>Some</u> of the new N_2 reacts with some of the H_2, (decreasing n_{H2}), producing more NH_3 (increasing n_{NH3}). There's still some of the new N_2, i.e., n_{N2} still increases somewhat.

Example: p + e ↔ H at 6000K

We pick this reaction because each component (proton, electron, hydrogen atom) has no internal modes (except spin, not important here) so we can write down the component μ's easily.

What is the relation between n_p and n_H at T = 6000 K?

Solution

We pick this reaction because each component (proton, electron, hydrogen atom) has no internal modes (except spin, not important here) so we can write down the component μ's easily.

What is the relation between n_p and n_H at T = 6000 K?

Start with the exact equilibrium rule:

$$\mu_p + \mu_e = \mu_H$$

Now use that these are almost ideal monatomic components, (as long as the density is low).

$$kT \ln\left(\frac{n_p}{n_{pQ}}\right) + kT \ln\left(\frac{n_e}{n_{eQ}}\right) = kT \ln\left(\frac{n_H}{n_{HQ}}\right) - \Delta$$

Also: $n_p = n_e$ $\Leftarrow$ because they are produced in pairs.

So: $\left(\frac{n_p}{n_{pQ}}\right)\left(\frac{n_e}{n_{eQ}}\right) = \left(\frac{n_H}{n_{HQ}}\right)e^{-\Delta/kT}$

$$n_p^2 = \left(n_{pQ} n_{eQ}\right)\left(\frac{n_H}{n_{HQ}}\right) \approx n_{eQ} n_H e^{-\Delta/kT}$$

because $n_{pQ} \approx n_{HQ}$

Now use: $\Delta = 13.6\text{eV}$ and $n_{eQ} = 2 \times (1.2 \times 10^{27}\ \text{m}^{-3})$ at 6000K

$$n_p^2 \approx 10^{16}\, m^{-3} n_H \text{ at 6000 K}$$

On the Sun: $\rho \sim \rho_{H2O}$. So, $n_H \sim 6 \times 10^{29}/\text{m}^3$.

$\Rightarrow n_p \sim 7 \times 10^{22}/\text{m}^3$, not very large.

Only 1 in 10^7 ionized.

ACT 2

The temperature of the Sun actually varies a great deal, from ~5700K at the surface, to ~10^7 K in the interior.

1) For what approximate temperature will we have $n_p \sim n_H$?

    A) 10,000 K   B) 60,000 K   C) 160,000 K   D) 6 x 10^6 K

Solution

The temperature of the Sun actually varies a great deal, from ~5700K at the surface, to ~10^7 K in the interior.

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    As a rough estimate, we set kT = 13.6 eV → T = 160,000 K

Non-monatomic Gases

Formation of H_2 from hydrogen atoms:
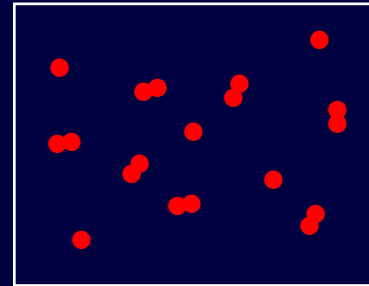
$H_2 \leftrightarrow 2H$, so $\mu_{H2} = 2\mu_H$.

Equilibrium condition:

$$\frac{n_{H_2}}{n_H^2} = K(T), \text{ where } K(T) = \frac{n_{Q_{H2}}}{n_{Q_H}^2} e^{+\Delta/kT}$$

$\Delta = H_2$ binding energy $= 4$ eV

$T = 1000$ K

We can use n_{QH}, because it's monatomic.

We don't know how to calculate n_{QH2}, because it is diatomic and has extra U and S.

However, we saw last week that we can estimate the effect that H_2 being diatomic has on μ_{H2}, namely it reduces it.

Act 2: Formation of H_2

We have: $\dfrac{n_{H_2}}{n_H^2} = K(T)$

1) What happens to n_H if we decrease n_{H2}?

    A) Decrease   B) Increase   C) Increase, then decrease

2) What happens to n_H/n_{H2} if we decrease n_{H2}?

    A) Decrease   B) Increase   C) Increase, then decrease

Solution

We have: $\dfrac{n_{H_2}}{n_H^2} = K(T)$

1) What happens to n_H if we decrease n_{H2}?

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Since $n_H \propto \sqrt{n_{H2}}$, decreasing n_{H2} decreases n_H.
Makes sense: The overall density is reduced.

2) What happens to n_H/n_{H2} if we decrease n_{H2}?

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We have: $\dfrac{n_{H_2}}{n_H^2} = K(T)$

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We can also write it like this: $\dfrac{n_{H_2}^2}{n_H^2} = n_{H_2} K(T) \Rightarrow \dfrac{n_{H_2}}{n_H} = \sqrt{n_{H_2} K(T)} \Rightarrow \dfrac{n_H}{n_{H_2}} \propto \dfrac{1}{\sqrt{n_{H_2}}}$

Thus, decreasing n_{H2} increases the fraction of free atoms.
$2H \to H_2$ requires that two atoms meet, while
$H_2 \to 2H$ only requires a single molecule.
At low density, the rate of the second process is higher, shifting equilibrium to more H.
At a given T, the fraction of atoms increases at lower molecule density!
There are more H atoms in outer space than H_2 molecules. Why?
Two particles (H + H) have more <u>entropy</u> than one particle (H_2). Entropy maximization dominates the tendency of atoms to bind!!!

Phase Transitions

Roadmap:

We'll start by looking at a simple model of atoms on surfaces, and discover that, depending on the temperature, the atoms prefer to be bound or to be flying free.

This is related to the common observation that materials can be found in distinct phases: E.g., solid, liquid, gas.

We'll learn how equilibria between these phases work.

Then we'll go back and try to understand why distinct phases exist in the first place.
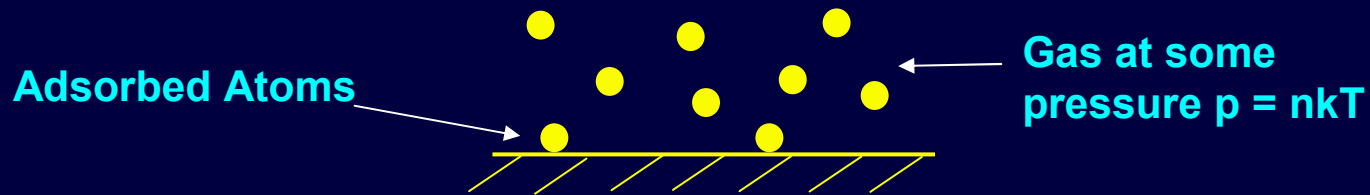
Applications of Surface Chemistry

Catalysis -- purify engine exhaust
Oxidation of surfaces
Fabrication of high quality films
Binding of O_2 gas to hemoglobin and myoglobin in your body

......

Adsorbed Atoms

Gas at some pressure p = nkT

In equilibriuim: $\mu_g = \mu_s$

Chemical potential of the gas:

$$\mu_g = kT \ \ln\left(\frac{n}{\tilde{n}_Q}\right) = kT \ln\left(\frac{nkT}{\tilde{n}_Q kT}\right) = kT \ \ln\left(\frac{p}{p_Q}\right)$$

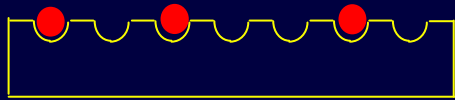**where we've defined**

$$\boxed{p_Q \equiv \tilde{n}_Q kT}$$

p_Q, the "quantum pressure", is the pressure it would take (hypothetically) to compress an ideal gas to the quantum density, so that there was 1 particle per "quantum cell".

Chemical potential of the surface:

$$\mu_s = \frac{dF_s}{dN_s} \quad \text{with} \quad F_s = U_s - TS_s = ?$$

Adsorption of Atoms on a Surface

M = # (single occupancy) binding sites on the surface

Δ = binding energy of an atom on site

N_s = number of bound atoms

F_s = Free energy of bound atoms

$$F_s = U_s - TS_s = -N_s\Delta - kT\ln(\Omega)$$

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

Calculate the chemical potentials:

Bound atoms:

$$\frac{d(\ln\Omega)}{dN_s} = \ln\left(\frac{M-N_s}{N_s}\right), \text{ using } \frac{d(\ln N!)}{dN} = \ln N$$

$$\mu_s = \frac{dF_s}{dN_s} = -\Delta - kT\ln\left(\frac{M-N_s}{N_s}\right)$$

Atoms in the gas:

$$\mu_g = kT\,\ln\left(\frac{p}{p_Q}\right), \text{ where } p_Q = n_Q kT$$

Equilibrium:

$$\mu_s = \mu_g \implies \frac{M-N_s}{N_s} = \frac{p_Q}{p}e^{-\Delta/kT}$$

We could solve this equation for N_s, but …

Adsorption of Atoms (2)

… usually we want to know what fraction of the surface sites are occupied, for a given gas pressure p and temperature T:
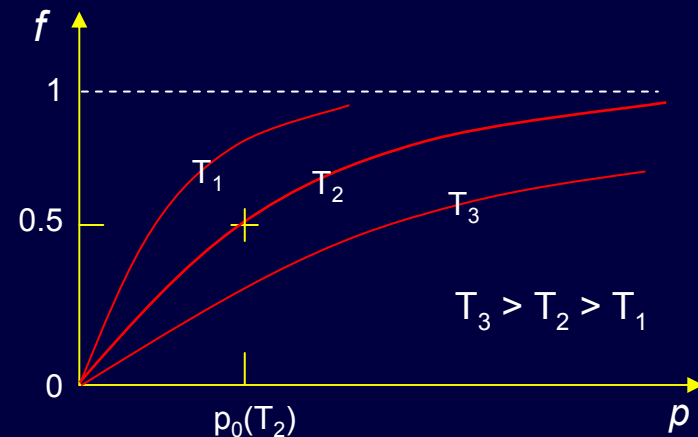
Using our result: $\dfrac{M - N_s}{N_s} = \dfrac{p_Q}{p} e^{-\Delta/kT} = \dfrac{p_0}{p}$, where $p_0 \equiv p_Q e^{-\Delta/kT}$

We obtain a simple relation for the fraction of occupied sites: $\boxed{f \equiv \dfrac{N_s}{M} = \dfrac{p}{p + p_o}}$

More atoms go onto the surface at high pressure, because μ_{gas} increases with pressure.

$p_o(T)$ is the characteristic pressure at which half the surface sites are occupied. It increases with temperature due to the Boltzmann factor.

Example: Adsorption of Atoms

At T = 300 K and p = 1 atm, it is observed that 50% of the binding sites on a particular metal surface are occupied. When the temperature is raised to 320 K at constant pressure, only 25% of the sites are occupied. (You may assume that p_Q is constant over this small temperature range.)

What is the binding energy of a site on the surface?

$k = 8.617 \times 10^{-5}$ eV/K

Solution

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$$f(300K) = \frac{1}{2} = \frac{1\,\text{Atm}}{1\,\text{Atm} + p_0(300K)} \quad \rightarrow$$

What is $p_0(320K)$?

$So:$

$$p_0(300K) = 1\,\text{Atm} = p_Q e^{-\Delta/k(300K)}$$

$$p_0(320K) = 3\,\text{Atm} = p_Q e^{-\Delta/k(320K)}$$

$$3 = e^{-(\Delta/k)(1/320 - 1/300)}$$

$$\Delta = k\ln(3)/(1/300 - 1/320) = 0.454 \text{ eV}$$

Act 3: Adsorption

1) At 10 atm, half the sites are occupied. What fraction are occupied at 0.1 atm?

    A) 1%   B) 11%   C) 90%

2) Keep the pressure constant, but increase T. What happens to f?

    A) Decrease   B) No effect   C) Increase

Solution

1) At 10 atm, half the sites are occupied. What fraction are occupied at 0.1 atm?

A) 1%   B) 11%   C) 90%

$$f = \frac{p}{p + p_0} = \frac{0.1}{0.1 + 10} = 9.9 \times 10^{-3} \approx 1\%$$

At lower pressure, gas atoms hit the surface less often.

2) Keep the pressure constant, but increase T. What happens to f?

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Solution

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Higher T:
$\Rightarrow$ higher p_Q and $e^{-\Delta/kT}$
$\Rightarrow$ p_0 increases $p_0 \equiv p_Q e^{-\Delta/kT}$
$\Rightarrow$ f decreases
Makes sense? More atoms have enough thermal energy to leave.

Example: Oxygen in blood

Your body needs to carry O_2 from the lungs out to tissues (called T in the reactions below), using some carrier molecule. Suppose it's myoglobin. If there are M myoglobin binding sites and N_B bound oxygen molecules, (and Δ is the binding energy of oxygen to myoglobin), we can analyze the transport of oxygen from lungs to tissues.

Solution

First look at the lungs. Ignore the effect of the oxygen on the myoglobin to which it binds, so it's just like the problem of adsorption by surface sites. Equilibrium is described by: $\mu_{gas} = \mu_{bound}$.

The fraction of occupied myoglobin sites is:
$$f = \frac{N_B}{M} = \frac{p_{O2}}{p_{02} + p_0}$$

We can't calculate p_0, but we know empirically that $f \approx 2/3$ in the lungs (where $p_{O2} = p_{lungs} \approx 0.19$ atm). That is, $p_0 \approx \frac{1}{2} p_{lungs}$

What happens in the tissue? p_0 is the same.
Empirically, $f \approx 1/3$, so $p_{tissue} \approx \frac{1}{2} p_0 \approx \frac{1}{4} p_{lungs}$.

About 1/3 of the myoglobin sites are used to transport oxygen to the tissues. Transport will occur as long as the O_2 pressure in the tissue is less than that in the lungs.

Next time

- Phase diagrams

- Latent heats

- Phase-transition fun