# Miscellaneous Notes



- The end is near – don't get behind.

- The PHYS 213 final exam times are
  * 8-10 AM, Friday, Dec. 13

  * 8-10 AM, Wednesday, Dec. 18

  Homework 6 is due <u>Tuesday</u>, Dec. 10 at 8 am. (NO late turn-in).

- Course Survey = 2 bonus points (accessible now in ByteShelf)

# Lecture 21:

## Chemical Equilibria

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:

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

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

$$= 0$$

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:

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

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 $\Delta$'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:

$\qquad$ aA + bB $\leftrightarrow$ cC

$\qquad$ RHS $\rightarrow$ numerator
$\qquad$ 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 | $aA + bB \ldots \leftrightarrow cC + dD \ldots$ | $a\mu_A + b\mu_B \ldots = c\mu_C + d\mu_D \ldots$ |

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 $\mu$ 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 $\Delta$'s) , so they must be included in the $\mu$'s. (dF/dN)

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

# But then, in phase transitions, why is usually only ONE stable phase?

- Ordinary chemical reaction equilibria:

  - *At low concentration $n_i$, $\mu_i$ drops without limit* (e.g. $kT\ln(n_i/n_T)$) until it matches the other $\mu$'s, at some particular ratio.

  - Therefore have positive concentrations of *every* possible molecular type.

    » true at fixed p or at fixed V

- Phase transitions:

  - *Each phase has a definite density* at a given (T,p) and hence a definite $\mu$, regardless of how much is present!

    - Adding material changes the *volume* of the phase, not the *density*, so $\mu$ *doesn't change*.

- Therefore at most (T, p) only ONE phase, with lowest $\mu$, is stable.

  - At special (T, p), two can have the same $\mu$, so they can coexist in any ratio.

  - Under constant V conditions, p, and thus $\mu$, depends on the *amounts* of the phases, and thus there are some coexistence ranges, e.g., in a pressure cooker.

# ACT 1:
# Equilibrium in the Ammonia Reaction

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

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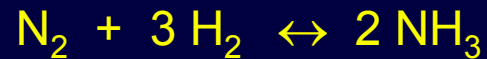
1) Insert the correct superscripts and subscripts in the equilibrium equation:

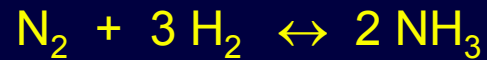$$\frac{n_{(\ )}^{(\ )} n_{(\ )}^{(\ )}}{n_{(\ )}^{(\ )} n_{(\ )}^{(\ )}} = K(T)$$

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:

$$\frac{n_{(NH_3)}^{(2)} \, n_{(\phantom{X})}^{(\phantom{X})}}{n_{(N_2)}^{(1)} \, n_{(H_2)}^{(3)}} = K(T)$$
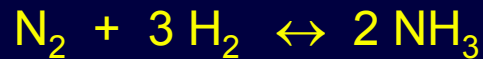
Of course, you could write the whole thing upside down, with K'(T) = 1/K(T).

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

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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.

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 $\mu$'s easily, and exactly.

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 $\mu$'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: $n_p = n_e$ ⟸ because they are produced in pairs.

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

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

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

Now use: $\Delta$ = 13.6eV and $n_{eQ}$ = 2x(1.2x10$^{27}$ 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, $n_H \sim 6\times10^{29}$/m$^3$.

⟹ $n_p \sim 8 \times10^{22}$/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 <u>approximate</u> 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.

1) For what <u>approximate</u> 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

As a rough estimate, we set kT = 13.6 eV $\rightarrow$ 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:

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

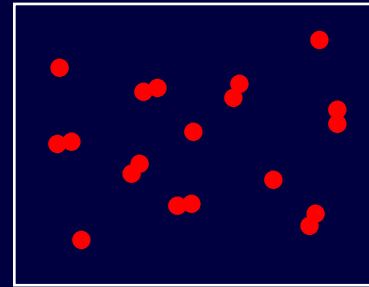$\Delta = H_2$ binding energy $= 4$ eV

$T = 1000$ K

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

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

However, we've already seen the effect that $H_2$ being diatomic has:

The addition of rotation/vibrational modes must
- increase $n_{QH2}$ – there are more possible states for the molecule when it could be rotating or vibrating than when it couldn't
- decrease F and $\mu$ – if they were not lowered when the molecules rotated, they would not rotate!

What does this do to equilibrium? $\mu_{H2}$ is now less than $2\mu_H$, so the reaction will proceed in the direction of increasing $n_{H2}$, until equality is restored.

# Act 3: 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: $\quad \dfrac{n_{H_2}}{n_H^2} = K(T)$

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

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

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 $n_{H2}$?

    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 $n_{H2}$?

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

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

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

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

Thus, decreasing $n_{H2}$ increases the fraction of free atoms.
    $2H \rightarrow H_2$ requires that two atoms meet, while
    $H_2 \rightarrow 2H$ 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!!!

# ACT 4: Oxygen in Solution

1) Consider oxygen dissolving in a liquid.  The reaction is $O_{2gas} \leftrightarrow O_{2liquid}$.
If you double the air pressure, keeping T constant, what happens to the density
of the dissolved $O_2$?  (Assume that the liquid itself is unaffected.)

   A) Density is halved     B) Density is unchanged    C) Density is doubled

2) Now consider $CO_2$ being dissolved according to the approximate reaction:
$CO_{2gas} \leftrightarrow CO_{2liquid}$ (here we neglect the chemistry that happens between the
$CO_2$ and water after the dissolving occurs). If we increase the temperature,
what will happen to the amount of $CO_2$ that can be 'kept' in the water?

   A) $CO_{2liquid}$ increases     B) $CO_{2liquid}$ stays the same C) $CO_{2liquid}$ decreases

# Solution

1) Consider oxygen dissolving in a liquid.  The reaction is $O_{2gas} \leftrightarrow O_{2liquid}$.
If you double the air pressure, keeping T constant, what happens to the density of the dissolved $O_2$?  (Assume that the liquid itself is unaffected.)

   A) Density is halved     B) Density is unchanged    C) Density is doubled

$$\frac{n_{gas}}{n_{liquid}} = K(T)$$     K remains unchanged, so $n_{liquid}$ must double.

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   A) $CO_{2liquid}$ increases     B) $CO_{2liquid}$ stays the same  C) $CO_{2liquid}$ decreases

The $CO_2$ has more entropy in the atmosphere than in the water. So at
high temperature that's where we find the $CO_2$. This means that global
warming is doubly bad – it reduces the capacity of the ocean for $CO_2$,
just when we'd like the ocean to take up more.

**CO2 pressure temperature dependence**

◆ water
■ carbonated

Pressure − 14 psi (psi) vs. Temperature (celcius)
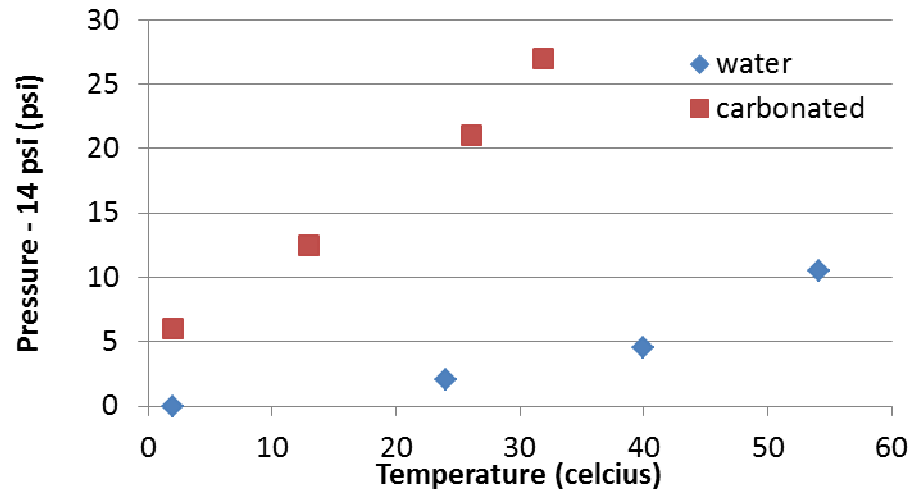
# Synchronous Change of Atmospheric $CO_2$ and Antarctic Temperature During the Last Deglacial Warming

F. Parrenin,[1]* V. Masson-Delmotte,[2] P. Köhler,[3] D. Raynaud,[1] D. Paillard,[2] J. Schwander,[4] C. Barbante,[5,6] A. Landais,[2] A. Wegner,[3]† J. Jouzel[2]

Understanding the role of atmospheric $CO_2$ during past climate changes requires clear knowledge of how it varies in time relative to temperature. Antarctic ice cores preserve highly resolved records of atmospheric $CO_2$ and Antarctic temperature for the past 800,000 years. Here we propose a revised relative age scale for the concentration of atmospheric $CO_2$ and Antarctic temperature for the last deglacial warming, using data from five Antarctic ice cores. We infer the phasing between $CO_2$ concentration and Antarctic temperature at four times when their trends change abruptly. We find no significant asynchrony between them, indicating that Antarctic temperature did not begin to rise hundreds of years before the concentration of atmospheric $CO_2$, as has been suggested by earlier studies.

Analyses of polar ice cores have shown that the concentration of atmospheric $CO_2$ (a$CO_2$) and surface air temperature are closely related and that they have risen and fallen in tandem over most of the past 800,000 years. However, whether changes of temperature occurred first and ha[...] been have been topi[...] sy. The most highly [...] the last deglacial wa[...] from the European [...] tarctica (EPICA) D[...] In this record, a$CO_2$ [...] temperature (AT) by [...] of TI, in agreement [...] Vostok and Taylor I[...] tified a lag of 600 ±[...]