

# 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 Tuesday, Dec. 10 at 8 am. (NO late turn-in).

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

# Lecture 21:

## Chemical Equilibria

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

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:

$$\begin{aligned}\frac{dF}{dN_A} &= \frac{\partial F}{\partial N_A} + \frac{\partial F}{\partial N_B} \frac{dN_B}{dN_A} + \frac{\partial F}{\partial N_C} \frac{dN_C}{dN_A} \\ &= \frac{\partial F}{\partial N_A} + \frac{b}{a} \frac{\partial F}{\partial N_B} - \frac{c}{a} \frac{\partial F}{\partial N_C} \\ &= 0\end{aligned}\quad \text{using } \frac{dN_A}{a} = \frac{dN_B}{b} = -\frac{dN_C}{c}$$

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

\*Obviously we can have more or fewer species.

# Chemical Equilibrium (2)

Treating the components as ideal gases or solutes:

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

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

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

$K(T)$  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:



RHS  $\rightarrow$  numerator

LHS  $\rightarrow$  denominator

# Examples of Chemical Equilibrium

<u>Process</u>	<u>Reaction</u>	<u>Equilibrium condition</u>
Dissociation of H <sub>2</sub> molecules	$\text{H}_2 \leftrightarrow 2\text{H}$	$\mu_{\text{H}_2} = 2\mu_{\text{H}}$
Ionization of H atoms	$\text{H} \leftrightarrow \text{e} + \text{p}$	$\mu_{\text{H}} = \mu_{\text{e}} + \mu_{\text{p}}$
Synthesize ammonia	$\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$	$\mu_{\text{N}_2} + 3\mu_{\text{H}_2} = \mu_{\text{NH}_3}$
General reaction	$a\text{A} + b\text{B} \dots \leftrightarrow c\text{C} + d\text{D} \dots$	$a\mu_{\text{A}} + b\mu_{\text{B}} \dots = c\mu_{\text{C}} + d\mu_{\text{D}} \dots$

For the monatomic gases (circled) you can use  $n_{\text{T}} = n_{\text{Q}}$ .

The others are more complicated, and we won't deal with it here.

However, remember that  $n_{\text{T}}$  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:

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

# 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:



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  $\text{N}_2$  molecules. What will happen?

A) Make more  $\text{NH}_3$ .    B) Dissociate more  $\text{NH}_3$ .    C) Nothing.



# Solution

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



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

$$\frac{n_{(\text{NH}_3)}^{(2)} n_{(\text{H}_2)}^{(3)}}{n_{(\text{N}_2)}^{(1)}} = K(T)$$

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  $\text{N}_2$  molecules. What will happen?

A) Make more  $\text{NH}_3$ .    B) Dissociate more  $\text{NH}_3$ .    C) Nothing.

# Solution

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



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

$$\frac{n_{(\text{NH}_3)}^{(2)} n_{(\text{H}_2)}^{(3)}}{n_{(\text{N}_2)}^{(1)}} = K(T)$$

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  $\text{N}_2$  molecules. What will happen?

A) Make more  $\text{NH}_3$ .    B) Dissociate more  $\text{NH}_3$ .    C) Nothing.

You've decreased the density ratio. To restore it,  $n_{\text{NH}_3}$  must increase and/or  $n_{\text{H}_2}$  must decrease. Some of the new  $\text{N}_2$  reacts with some of the  $\text{H}_2$ , (decreasing  $n_{\text{H}_2}$ ), producing more  $\text{NH}_3$  (increasing  $n_{\text{NH}_3}$ ). There's still some of the new  $\text{N}_2$ , i.e.,  $n_{\text{N}_2}$  still increases somewhat.

# Example: $p + e \rightleftharpoons H$ 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:  $n_p = n_e$   $\Leftarrow$  because they are produced in pairs.

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

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

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

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

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

On the Sun:  $\rho \sim \rho_{\text{H}_2\text{O}}$ .  
So,  $n_H \sim 6 \times 10^{29} / \text{m}^3$ .

$\Rightarrow n_p \sim 8 \times 10^{22} / \text{m}^3$ ,  
not very large.

Only 1 in  $10^7$  ionized.

# ACT 2

The temperature of the Sun actually varies a great deal, from  $\sim 5700\text{K}$  at the surface, to  $\sim 10^7\text{ K}$  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)  $6 \times 10^6\text{ K}$

# Solution

The temperature of the Sun actually varies a great deal, from  $\sim 5700\text{K}$  at the surface, to  $\sim 10^7\text{ K}$  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)  $6 \times 10^6\text{ K}$

As a rough estimate, we set  $kT = 13.6\text{ eV} \rightarrow T = 160,000\text{ K}$

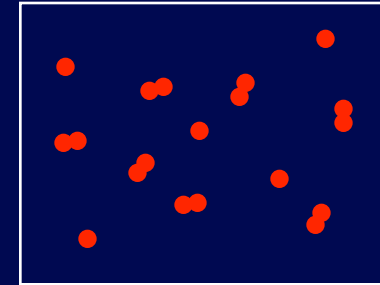
# Non-monatomic Gases

Formation of  $H_2$  from hydrogen atoms:

$$H_2 \leftrightarrow 2H, \text{ so } \mu_{H_2} = 2\mu_H.$$

Equilibrium condition:

$$\frac{n_{H_2}}{n_H^2} = K(T), \text{ where } K(T) = \frac{n_{QH_2}}{n_{QH}^2} e^{+\Delta/kT}$$



$\Delta = H_2$  binding energy = 4 eV

$T = 1000$  K

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

We don't know how to calculate  $n_{QH_2}$ , because it's diatomic and has extra U and S.

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

- increase  $n_{QH_2}$  – 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?  $\mu_{H_2}$  is now less than  $2\mu_H$ , so the reaction will proceed in the direction of increasing  $n_{H_2}$ , until equality is restored.

# Act 3: Formation of $H_2$

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

1) What happens to  $n_H$  if we decrease  $n_{H_2}$ ?

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

2) What happens to  $n_H/n_{H_2}$  if we decrease  $n_{H_2}$ ?

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



# Solution

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

1) What happens to  $n_H$  if we decrease  $n_{H_2}$ ?

A) Decrease

B) Increase

C) Increase, then decrease

Since  $n_H \propto \sqrt{n_{H_2}}$ , decreasing  $n_{H_2}$  decreases  $n_H$ .  
Makes sense: The overall density is reduced.

2) What happens to  $n_H/n_{H_2}$  if we decrease  $n_{H_2}$ ?

A) Decrease

B) Increase

C) Increase, then decrease

# Solution

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

1) What happens to  $n_H$  if we decrease  $n_{H_2}$ ?

A) Decrease

B) Increase

C) Increase, then decrease

Since  $n_H \propto \sqrt{n_{H_2}}$ , decreasing  $n_{H_2}$  decreases  $n_H$ .  
Makes sense: The overall density is reduced.

2) What happens to  $n_H/n_{H_2}$  if we decrease  $n_{H_2}$ ?

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  $n_{H_2}$  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 entropy 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  $\text{O}_{2\text{gas}} \leftrightarrow \text{O}_{2\text{liquid}}$ . If you double the air pressure, keeping T constant, what happens to the density of the dissolved  $\text{O}_2$ ? (Assume that the liquid itself is unaffected.)

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

2) Now consider  $\text{CO}_2$  being dissolved according to the approximate reaction:  $\text{CO}_{2\text{gas}} \leftrightarrow \text{CO}_{2\text{liquid}}$  (here we neglect the chemistry that happens between the  $\text{CO}_2$  and water after the dissolving occurs). If we increase the temperature, what will happen to the amount of  $\text{CO}_2$  that can be 'kept' in the water?

- A)  $\text{CO}_{2\text{liquid}}$  increases      B)  $\text{CO}_{2\text{liquid}}$  stays the same      C)  $\text{CO}_{2\text{liquid}}$  decreases

# Solution

1) Consider oxygen dissolving in a liquid. The reaction is  $O_{2\text{gas}} \leftrightarrow O_{2\text{liquid}}$ . 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

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

2) Now consider  $CO_2$  being dissolved according to the approximate reaction:  $CO_{2\text{gas}} \leftrightarrow CO_{2\text{liquid}}$  (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)  $CO_{2\text{liquid}}$  increases      B)  $CO_{2\text{liquid}}$  stays the same      C)  $CO_{2\text{liquid}}$  decreases

# Solution

1) Consider oxygen dissolving in a liquid. The reaction is  $O_{2\text{gas}} \leftrightarrow O_{2\text{liquid}}$ . 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

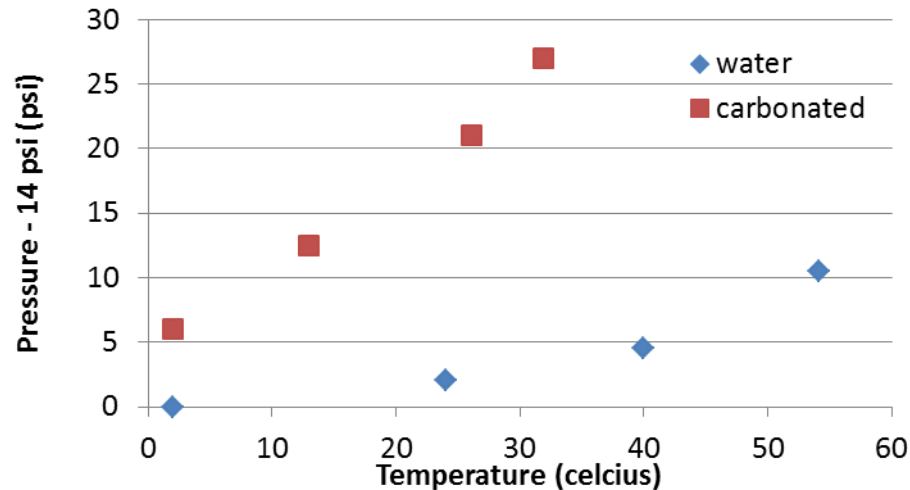
$$\frac{n_{\text{gas}}}{n_{\text{liquid}}} = K(T) \quad K \text{ remains unchanged, so } n_{\text{liquid}} \text{ must double.}$$

2) Now consider  $CO_2$  being dissolved according to the approximate reaction:  $CO_{2\text{gas}} \leftrightarrow CO_{2\text{liquid}}$  (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)  $CO_{2\text{liquid}}$  increases      B)  $CO_{2\text{liquid}}$  stays the same      C)  $CO_{2\text{liquid}}$  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.

## CO<sub>2</sub> pressure temperature dependence



# Synchronous Change of Atmospheric CO<sub>2</sub> and Antarctic Temperature During the Last Deglacial Warming

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

Understanding the role of atmospheric CO<sub>2</sub> 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<sub>2</sub> and Antarctic temperature for the past 800,000 years. Here we propose a revised relative age scale for the concentration of atmospheric CO<sub>2</sub> and Antarctic temperature for the last deglacial warming, using data from five Antarctic ice cores. We infer the phasing between CO<sub>2</sub> 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<sub>2</sub>, as has been suggested by earlier studies.

Analyses of polar ice cores have shown that the concentration of atmospheric CO<sub>2</sub> (aCO<sub>2</sub>) 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 how they have been topically. The most highly resolved records of the last deglacial warming come from the European ice core (EPICA) Dome C. In this record, aCO<sub>2</sub> and temperature (AT) by the time of TI, in agreement with Vostok and Taylor. This indicates a lag of 600 ±

<sup>1</sup>Laboratoire de Glaciologie (CNRS/UJF), Grenoble, France. <sup>2</sup>Climate and Environment, Yvette, France. <sup>3</sup>Alfred Wegener Research, Bremerhaven, Germany. <sup>4</sup>University of Bern, Bern, Switzerland. <sup>5</sup>Sciences, University of Venice, Venice, Italy. <sup>6</sup>Dynamics of Environmental

\*Corresponding author. †Present address: Byrd Polar Research Station, University of Columbus, O