

# Chemistry 2000 Slide Set 11: Chemical equilibrium

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# Thermodynamic criterion for equilibrium

- Recall that under given reaction conditions (concentrations of reactants and products),

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$$

- If  $\Delta_r G_m < 0$ , the reaction is thermodynamically allowed as written.
- If  $\Delta_r G_m > 0$ , the reverse of the reaction is thermodynamically allowed.
- What happens if  $\Delta_r G_m = 0$ ?
  - Neither the forward nor reverse direction of the reaction is thermodynamically allowed, so the reaction is **at equilibrium**.

# The equilibrium constant

- At equilibrium,

$$\begin{aligned}\Delta_r G_m &= \Delta_r G_m^\circ + RT \ln Q = 0 \\ \therefore \Delta_r G_m^\circ &= -RT \ln Q\end{aligned}$$

- This last equation implies that there is a fixed value of the reaction quotient  $Q$  when we reach equilibrium.
- We call this value the **equilibrium constant  $K$** .  
Thus,

$$\Delta_r G_m^\circ = -RT \ln K$$

- For a given reaction,  $K$  is a number that depends only on the temperature.
- At equilibrium,  $Q = K$ .

- If we know  $K$ , we can calculate the **standard** free energy change for a reaction by

$$\Delta_r G_m^\circ = -RT \ln K$$

- We can also rearrange this equation to calculate  $K$  from  $\Delta_r G_m^\circ$ :

$$\ln K = -\frac{\Delta_r G_m^\circ}{RT}$$
$$\therefore K = \exp\left(-\frac{\Delta_r G_m^\circ}{RT}\right)$$

$$[\exp(x) = e^x]$$

$$\Delta_r G_m^\circ = -RT \ln K$$

**Important:**  $K$  is related to the **standard** free energy change  $\Delta_r G_m^\circ$  (obtained from tables of standard free energies of formation), **not** to  $\Delta_r G_m$ , which is zero at equilibrium.

# Thinking in terms of $Q$ and $K$

- Roughly,  $Q = \frac{\text{products}}{\text{reactants}}$ .
- If  $Q < K$ , then  $Q$  needs to grow to reach equilibrium.
- $Q$  increases if we make more products and consume reactants.

**Conclusion:** If  $Q < K$ , a reaction is thermodynamically allowed as written.

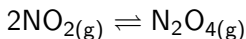
**Converse:** If  $Q > K$ , the reverse of the reaction is thermodynamically allowed.

# Conditions for thermodynamic feasibility

$\Delta_r G_m < 0 \iff Q < K \iff$  reaction  
thermodynamically allowed

$\Delta_r G_m = 0 \iff Q = K \iff$  equilibrium

$\Delta_r G_m > 0 \iff Q > K \iff$  reverse reaction  
thermodynamically allowed

Example: Dimerization of NO<sub>2</sub>

$$\begin{aligned}\Delta_r G_m^\circ &= \Delta_f G^\circ(\text{N}_2\text{O}_4, \text{g}) - 2\Delta_f G^\circ(\text{NO}_2, \text{g}) \\ &= 97.79 - 2(51.3) \text{ kJ/mol} = -4.8 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}K &= \exp\left(-\frac{\Delta_r G_m^\circ}{RT}\right) \\ &= \exp\left(-\frac{-4.8 \times 10^3 \text{ J/mol}}{(8.314 463 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) \\ &= 6.96\end{aligned}$$

(Note the double negative in the exponential.)



- Suppose that, at some particular point in time,  $p_{\text{NO}_2} = 0.4$  bar and  $p_{\text{N}_2\text{O}_4} = 1.8$  bar.
- Is the reaction thermodynamically allowed under these conditions?

$$\begin{aligned} Q &= \frac{a_{\text{N}_2\text{O}_4}}{(a_{\text{NO}_2})^2} \\ &= \frac{p_{\text{N}_2\text{O}_4}/p^\circ}{(p_{\text{NO}_2}/p^\circ)^2} \\ &= \frac{1.8}{(0.4)^2} = 11 \\ Q &> K = 6.96 \end{aligned}$$

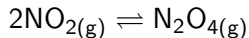
**Conclusion:** The reaction will run backwards,  
i.e.  $\text{N}_2\text{O}_4$  will dissociate into  $\text{NO}_2$ .

- We could have come to the same conclusion by calculating  $\Delta_r G_m$ :

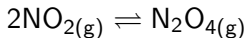
$$\begin{aligned}\Delta_r G_m &= \Delta_r G_m^\circ + RT \ln Q \\ &= -4.8 \text{ kJ/mol} + (8.314 463 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &\quad \times (298.15 \text{ K}) \ln(11) \\ &= 1.2 \text{ kJ/mol} > 0,\end{aligned}$$

from which we also conclude that the reverse reaction is thermodynamically allowed.

# Calculating an equilibrium mixture



- For the composition given above (0.4 bar  $\text{NO}_2$ , 1.8 bar  $\text{N}_2\text{O}_4$ , we know that the reaction will run backwards, dissociating  $\text{N}_2\text{O}_4$ , until equilibrium is reached.
- What is the equilibrium composition?



- Use an Initial/Change/Equilibrium (ICE) table to figure out the equilibrium composition.

	NO <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>
I	0.4	1.8
C	2x	-x
E	0.4 + 2x	1.8 - x

- Substitute into the equilibrium relationship:

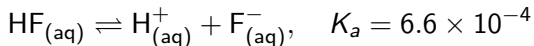
$$K = 6.96 = \frac{a_{\text{N}_2\text{O}_4}}{a_{\text{NO}_2}^2} = \frac{1.8 - x}{(0.4 + 2x)^2}$$

and solve for  $x$ .

- Find  $x = 0.0507$ , which gives  $p_{\text{NO}_2} = 0.50$  bar and  $p_{\text{N}_2\text{O}_4} = 1.75$  bar.

# Acid ionization constants

The acid ionization constant  $K_a$  of (e.g.) hydrofluoric acid is the equilibrium constant for the reaction



**Problem:** Calculate  $\Delta_f G^\circ(\text{HF}, \text{aq})$  given  
 $\Delta_f G^\circ(\text{F}_{(\text{aq})}^-) = -281.52 \text{ kJ/mol}$ .

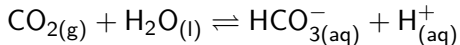
**Answer:**  $\Delta_f G^\circ(\text{HF}, \text{aq}) = -299.7 \text{ kJ/mol}$

# pH

Important definition:  $\text{pH} = -\log_{10}(a_{\text{H}^+})$

# pH of water in equilibrium with atmospheric CO<sub>2</sub>

- CO<sub>2</sub> in the atmosphere currently has a concentration of approximately 411 ppm.
- CO<sub>2</sub> reacts with water according to



- Equilibration with CO<sub>2</sub> therefore acidifies water.
- What is the pH of water that has been equilibrated with the atmosphere at 25 °C?

# pH of water in equilibrium with atmospheric CO<sub>2</sub>

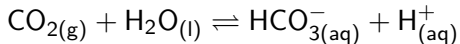
Conversion from ppm to bar

- ppm can refer to mass or mole fraction.
- In the case of atmospheric gases, the concentration is a mole fraction.
- 411 ppm means that for every million molecules in the atmosphere, approximately 411 are CO<sub>2</sub> molecules.
- Given the proportionality between  $n$  and  $p$ , this means that

$$p_{\text{CO}_2} = \frac{411}{10^6} (1.013\,25 \text{ bar}) = 4.16 \times 10^{-4} \text{ bar}$$

at average sea level pressure.



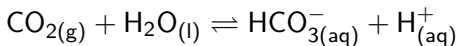
pH of water in equilibrium with atmospheric CO<sub>2</sub>

	$\Delta_f G^\circ / \text{kJ mol}^{-1}$
$\text{CO}_{2(\text{g})}$	-394.37
$\text{HCO}_{3(\text{aq})}^-$	-586.8
$\text{H}_2\text{O}_{(\text{l})}$	-237.140

From these data, calculate

$$\Delta_r G^\circ = 44.7 \text{ kJ mol}^{-1}$$

$$K = 1.47 \times 10^{-8}$$

pH of water in equilibrium with atmospheric CO<sub>2</sub>

$$K = \frac{(a_{\text{HCO}_3^-})(a_{\text{H}^+})}{(a_{\text{CO}_2})(a_{\text{H}_2\text{O}})}$$

- Take  $a_{\text{H}_2\text{O}} \approx 1$ .
- $a_{\text{CO}_2} = p_{\text{CO}_2}/p^\circ = 4.16 \times 10^{-4}$
- If we start with pure water, then  $a_{\text{HCO}_3^-} = a_{\text{H}^+}$ .

- Solve

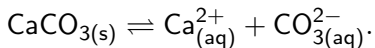
$$1.47 \times 10^{-8} = \frac{(a_{\text{H}^+})^2}{(4.16 \times 10^{-4})}$$

to get  $a_{\text{H}^+} = 2.47 \times 10^{-6}$ .

- $\text{pH} = -\log_{10} a_{\text{H}^+} = 5.61$

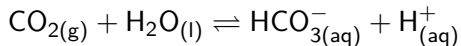
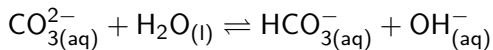
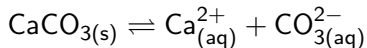
# Ocean acidification

- The foregoing calculation shows that surface water acidity is linked to atmospheric  $\text{CO}_2$  levels.
- More  $\text{CO}_2 \implies$  increased acidity
- Seawater is slightly alkaline due to equilibria involving carbonate minerals, notably



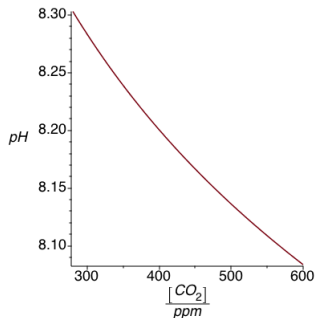
# Ocean acidification (continued)

- Key equilibria in sea water



# Ocean acidification (continued)

- Calculation of pH vs atmospheric  $\text{CO}_2$  pressure using only these equilibria:



(280 ppm = pre-industrial, 411 = current,  
600 = year 2100 if emissions continue at current levels)

# Ocean acidification (continued)

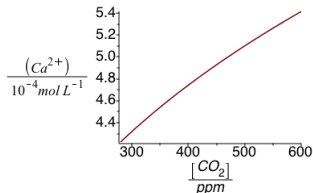
## Solubility of calcium carbonate

- These may not seem like large changes in pH, but

- 1 pH is a logarithmic scale.

Decrease by 0.1 pH units = increase in  $[H^+]$  by a factor of 1.26

- 2 Causes a large relative change in  $CaCO_3$  solubility:



- 13% increase in  $CaCO_3$  solubility from pre-industrial  $CO_2$  levels to now
- Problem for shellfish!

# Vapor pressure of a pure substance

- Imagine taking a pure substance (solid or liquid), putting it in an air-tight container, removing all the air, then letting it come to equilibrium.
- The equilibrium pressure reached in this experiment is the **vapor pressure** of the substance and is due to evaporation of the substance.

**Note:** It isn't really necessary to remove the air, but it makes the measurement easier.

**Also note** that if the partial pressure of a substance is lower than the (equilibrium) vapor pressure, it will evaporate. If, on the other hand, the partial pressure is higher than the vapor pressure, it will condense.

**Problem:** Calculate the vapor pressure of pure water at 25°C.

Species	$\Delta_f G^\circ / \text{kJ mol}^{-1}$
$\text{H}_2\text{O}_{(l)}$	-237.140
$\text{H}_2\text{O}_{(g)}$	-228.582

**Answer:**  $3.17 \times 10^{-2}$  bar



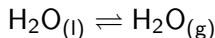
# Vapor pressures of solutions

- What about the vapor pressure of a solution?
- This could be due either to the solvent alone if the solute is (relatively) involatile (e.g. ionic compounds, sugar), or to a combination of the solvent and solute.

# Vapor pressures of solutions

## Raoult's law

- Let's start by looking at the **solvent**, again using water as an example.



$$K = \frac{a_g}{a_l} = \frac{p_{\text{H}_2\text{O}}/p^\circ}{X_{\text{H}_2\text{O}}}$$

- Note that  $K = p(\text{H}_2\text{O}, \text{pure})/p^\circ$ .

Notation:  $p(\text{H}_2\text{O}, \text{pure}) \equiv p_{\text{H}_2\text{O}}^\bullet$

$$\therefore p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^\bullet X_{\text{H}_2\text{O}}$$

or, in general,

$$p_{\text{solvent}} = p_{\text{solvent}}^\bullet X_{\text{solvent}}$$

- This equation is known as **Raoult's law**.

- Let's calculate the vapor pressure of an aqueous solution prepared by dissolving 1.875 mol of sodium sulfate in 1.000 kg of water at 60°C.
- The vapor pressure of pure water at this temperature is 149 Torr.

$$n_{\text{H}_2\text{O}} = \frac{1000 \text{ g}}{18.0153 \text{ g/mol}} = 55.51 \text{ mol}$$

$$n_{\text{Na}^+} = 2(1.875 \text{ mol}) = 3.750 \text{ mol}$$

$$n_{\text{SO}_4^{2-}} = 1.875 \text{ mol}$$

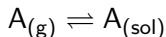
$$\begin{aligned} \therefore X_{\text{H}_2\text{O}} &= \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{Na}^+} + n_{\text{SO}_4^{2-}}} = \frac{55.51 \text{ mol}}{55.51 + 3.750 + 1.875 \text{ mol}} \\ &= 0.9080 \end{aligned}$$

$$\therefore p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^\bullet X_{\text{H}_2\text{O}} = (149 \text{ Torr})(0.9080) = 135 \text{ Torr}$$

# Vapor pressures of solutions

## Henry's law

- We can also consider the vapor pressure of a volatile solute or the solubility of a gas in a solvent using equilibrium theory.
- For either of these cases, we consider



$$K = \frac{a(A, sol)}{a(A, g)} = \frac{[A]/c^\circ}{p_A/p^\circ}$$

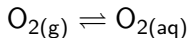
$$\therefore [A] = \frac{Kc^\circ}{p^\circ} p_A$$

or

$$[A] = k_H p_A$$

- This equation is known as **Henry's law**, and the constant  $k_H$  is called the Henry's law constant.

- Let us calculate the Henry's law constant for oxygen in water.
- The standard free energy of formation of an aqueous oxygen molecule is 16.35 kJ/mol.
- The process is



$$\Delta_r G^\circ = \Delta_f G^\circ(\text{O}_2, \text{aq}) - \Delta_f G^\circ(\text{O}_2, \text{g}) = 16.35 \text{ kJ/mol}$$

$$\therefore K = \exp\left(-\frac{\Delta_r G_m^\circ}{RT}\right)$$

$$= \exp\left(-\frac{16.35 \times 10^3 \text{ J/mol}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right)$$

$$= 1.366 \times 10^{-3}$$

$$k_H = \frac{Kc^\circ}{p^\circ} = 1.366 \times 10^{-3} \text{ mol L}^{-1} \text{ bar}^{-1}$$

- Suppose that the atmospheric pressure of oxygen is 0.18 bar (roughly the case in Lethbridge, 920 m above sea level).
- Then, in water at equilibrium with the atmosphere, we have

$$\begin{aligned}[\text{O}_2] &= k_H p_{\text{O}_2} \\ &= (1.366 \times 10^{-3} \text{ mol L}^{-1} \text{ bar}^{-1}) (0.18 \text{ bar}) \\ &= 2.5 \times 10^{-4} \text{ mol/L.}\end{aligned}$$

- That's (roughly) how much oxygen the fishies in the Oldman River have to live on.