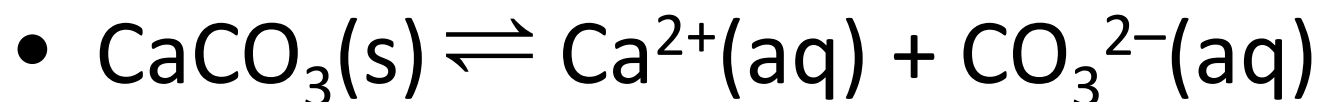


Chapter 9: Chemical Equilibria

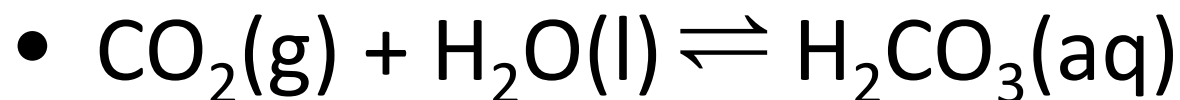
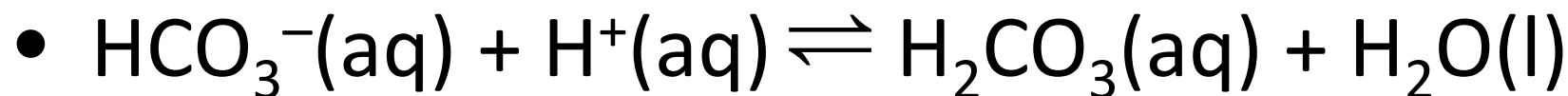
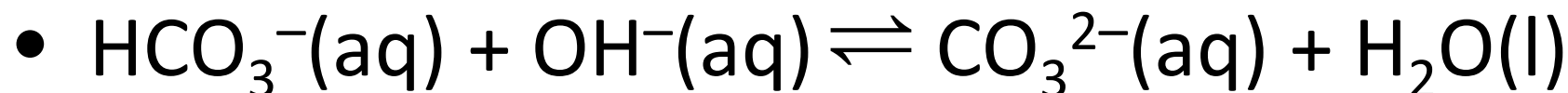
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Equilibrium between solid and dissolved calcium carbonate in the oceans

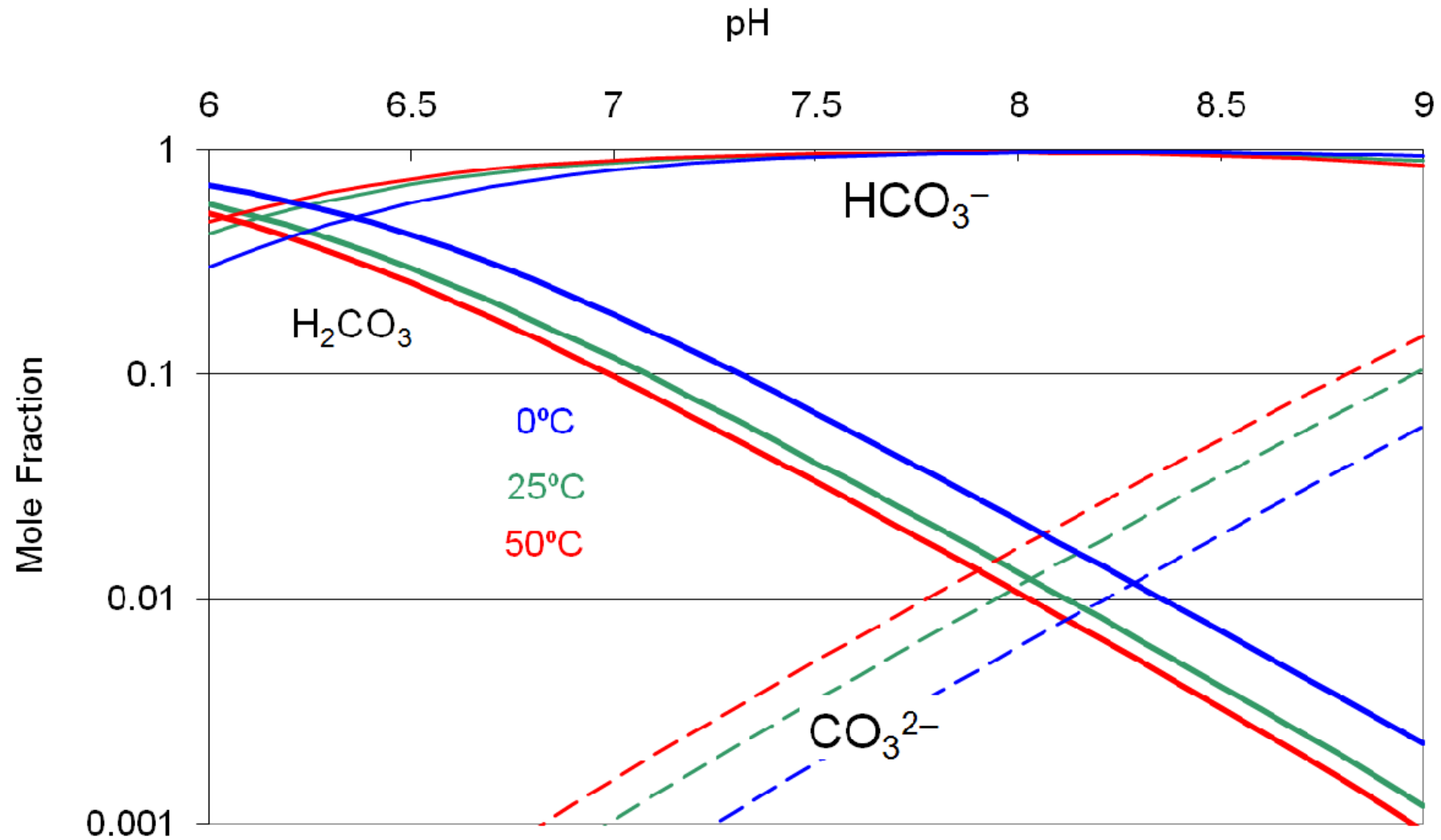


$$K = 4.5 \times 10^{-9} \text{ at } 25^\circ\text{C}$$



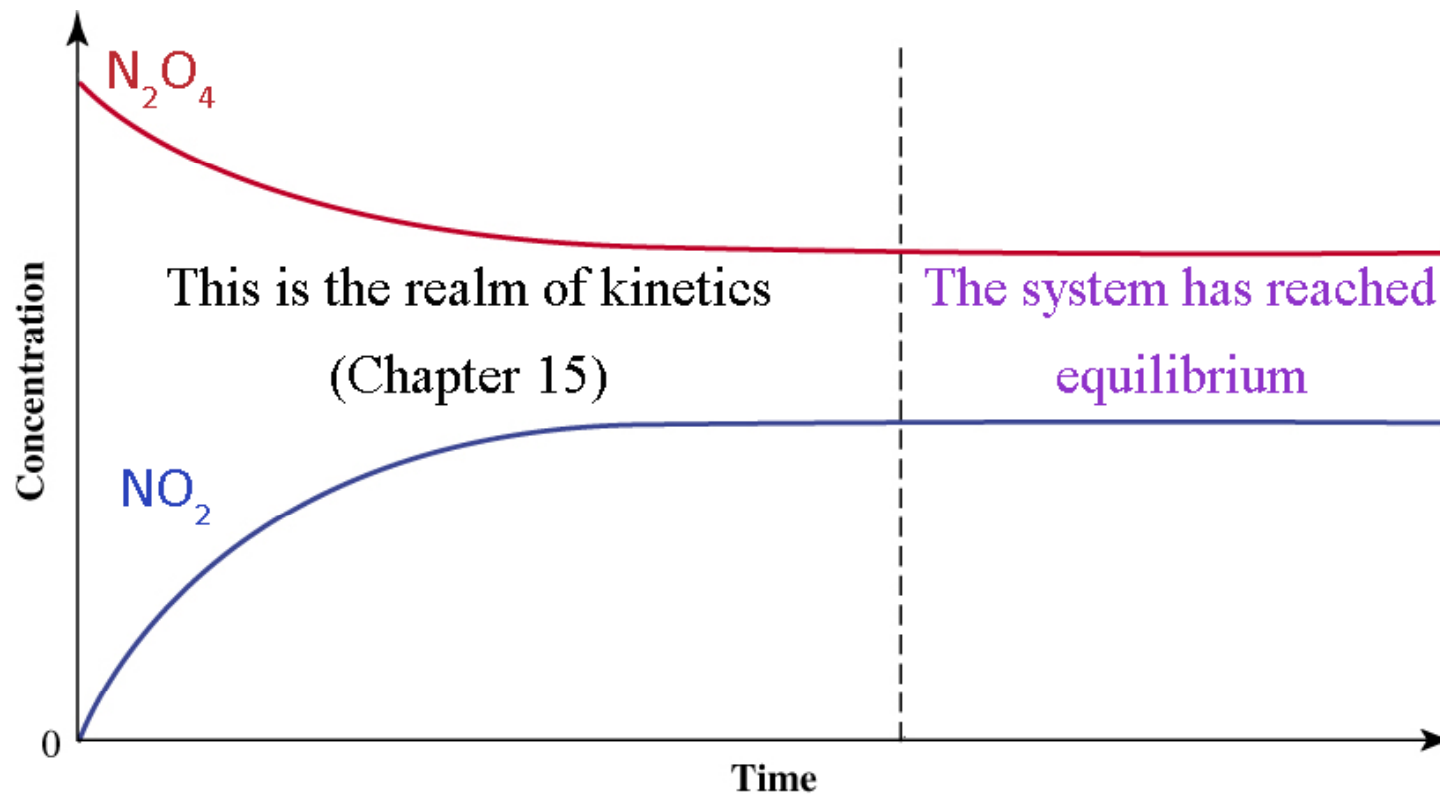
$$K = 0.002 \text{ at } 25^\circ\text{C}$$

Equilibrium between solid and dissolved calcium carbonate in the oceans



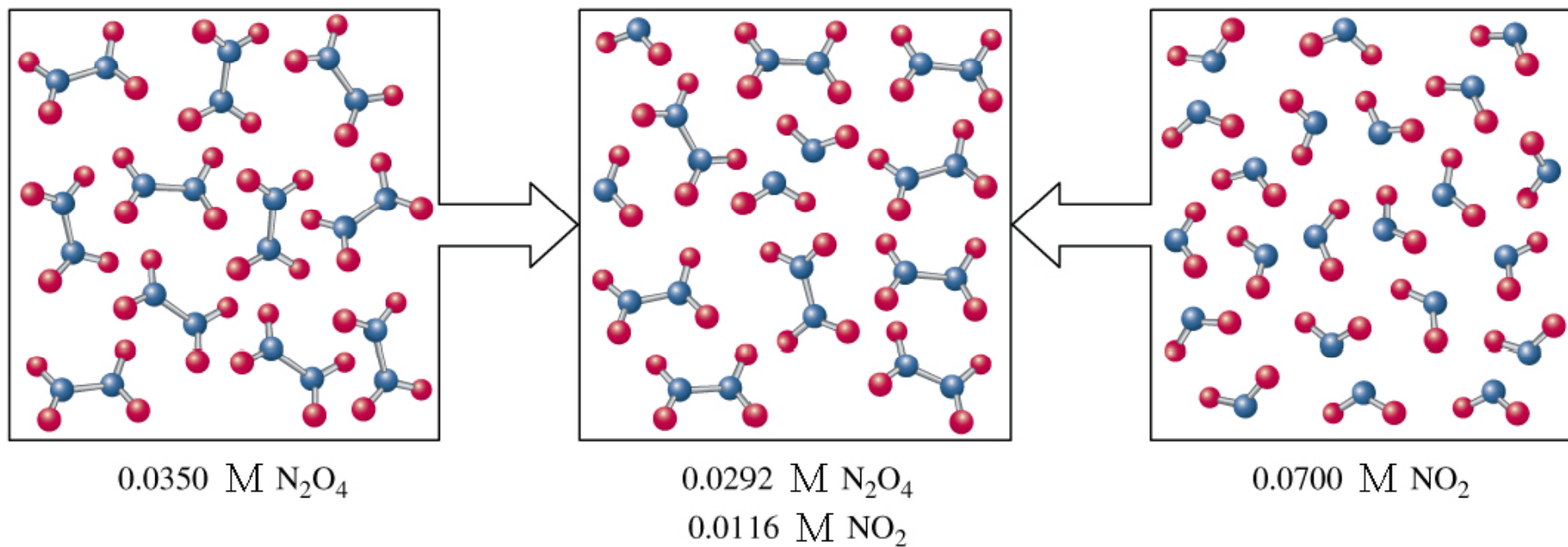
Equilibrium

- $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$
- Initial $[\text{NO}_2] = 0$



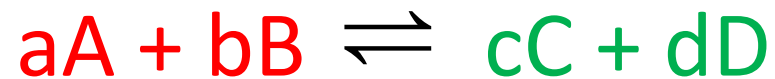
Equilibrium

Equilibrium



Quantifying Spontaneity

- For the general reaction:

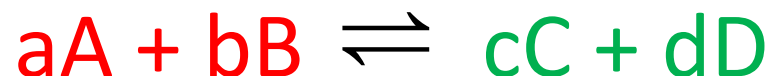


- The composition at equilibrium is given by a single number, K

$$K = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

Quantifying Spontaneity

- For the general reaction:



- The composition at equilibrium is given by a single number, K

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For solids or pure liquids appearing in the reaction, which have no pressure or concentration, we just put '1' in the equation

Actually...

$$K_p = \frac{\left(\frac{p_C}{p^\ominus}\right)^c \left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a \left(\frac{p_B}{p^\ominus}\right)^b}$$

- Where p^\ominus = standard pressure, 10^5 Pa

$$K_c = \frac{\left(\frac{[C]}{c^\ominus}\right)^c \left(\frac{[D]}{c^\ominus}\right)^d}{\left(\frac{[A]}{c^\ominus}\right)^a \left(\frac{[B]}{c^\ominus}\right)^b}$$

- Where c^\ominus = standard concentration, 1 M

Using K

- K for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is 0.106*.
- If we start with 1 atm** of dinitrogen tetroxide, what partial pressures do we have at equilibrium?

$$K_p = 0.106 = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} \quad \text{Let } p_{\text{NO}_2} = x$$

$$0.106 = \frac{x^2}{\left(1 - \frac{x}{2}\right)}$$

$$0.106 - 0.053x = x^2$$

$$x^2 + 0.053x - 0.106 = 0$$

$$x^2 = 0.300$$

Yes, you didn't just need to learn the quadratic formula for an exam and then forget it!

$$p_{\text{NO}_2} = 0.30 \text{ atm} \quad p_{\text{N}_2\text{O}_4} = 0.85 \text{ atm}$$

* At 15 °C

** Note I am using the approximation that 1 atm = 10⁵ Pa



K and Q



$$K = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

At equilibrium

$$Q = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

At any other point



K and Q



$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At equilibrium

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At any other point

K and Q

- If $Q < K$, the reaction has to go **forward**, more products required
- If $Q > K$, the reaction has to go **backward**, fewer products required
- And *now* we can talk about Gibbs Energy and equilibrium!

Gibbs Energy and Equilibrium

- The actual Gibbs Energy under non-standard conditions depends on Q:

$$\Delta G = \Delta G^{\ominus} + RT \ln Q$$

\ln = logarithm to base e
= $\log_{10} \times 2.30259\dots$

- When a reaction changes from spontaneous to non-spontaneous:
 - $Q = K$
 - $\Delta G = 0$
- So: $0 = \Delta G^{\ominus} + RT \ln K$

$$\Delta G^{\ominus} = -RT \ln K$$

Gibbs Energy and Equilibrium

- $8\text{Fe} + 6\text{NO}_2 \rightleftharpoons 4\text{Fe}_2\text{O}_3 + 3\text{N}_2$
- $\Delta S^\ominus = -723 \text{ JK}^{-1}\text{mol}^{-1}$
- $\Delta H^\ominus = -3492.0 \text{ kJ mol}^{-1}$
- $\Delta G^\ominus = -3492.0 \text{ kJ mol}^{-1} - 4500 \text{ K} \times (-723 \text{ JK}^{-1}\text{mol}^{-1})$
- $\Delta G^\ominus = -238.5 \text{ kJ mol}^{-1}$
- $\Delta G^\ominus = -RT \ln K$
- $\ln K = -\Delta G^\ominus / RT = 238500 \text{ J mol}^{-1} / (8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 4500 \text{ K})$
- $\ln K = 6.24$
- $K = e^{6.24} = 511$

So all these numbers are connected and we can predict exactly what proportions we will get from a chemical reaction under different conditions using thermodynamic data!

Gibbs Energy and Equilibrium

- $8\text{Fe} + 6\text{NO}_2 \rightleftharpoons 4\text{Fe}_2\text{O}_3 + 3\text{N}_2$
- $K = 511 = p_{\text{N}_2}^3 / p_{\text{NO}_2}^6$
- At a total pressure of 1 atm, how much NO_2 will be present at equilibrium under these conditions?
- Let $p_{\text{NO}_2} = x$
- $511 = (1-x)^3 / x^6$
- $x = 0.297$
- $p_{\text{NO}_2} = 0.297 \text{ atm}$

What's the best way to work out a complicated equation like this?

Anyone?

K_c and K_p

- If there is no change in the number of **moles of gas** in a reaction, $K_p = K_c$
- e.g., $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{CO}_2\text{(g)}$
 $n = 2 \qquad n = 2 \qquad \Delta n = 0; K_c = K_p$
- If there is, we have a slight problem – and one extra equation: $K_p = K_c (1000 \text{ RT}/p^\ominus)^{\Delta n}$
- e.g., $\text{H}_2\text{CO}_3\text{(s)} \rightleftharpoons \text{H}_2\text{O(s)} + \text{CO}_2\text{(g)}$
 $n = 0 \qquad n = 1 \qquad \Delta n = 1; K_c \neq K_p$

K_c and K_p

- $K_p = K_c (1000 \text{ RT}/p^\ominus)^{\Delta n}$
- $K_c = K_p (1000 \text{ RT}/p^\ominus)^{-\Delta n}$
- K_p for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is 0.106 at 15 °C
- What is K_c ?
- $K_c = K_p (1000 \text{ RT}/p^\ominus)^{-1}$ Since $\Delta n = 1$
- $K_c = 0.106 (1000 \text{ molm}^{-3} \times 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 288 \text{ K}/10^5 \text{ Pa})^{-1}$
- $K_c = 0.106/(23.9 \text{ m}^{-3}\text{JPa})$
- $K_c = 4.4 \times 10^{-3} (\cancel{\text{m}^{-3}.\text{kgm}^2\text{s}^{-2}}/(\cancel{\text{kgm}^{-1}\text{s}^{-2}}))$

Gibbs Energy and Equilibrium

$$\Delta G^{\ominus} = RT \ln K$$

- This is K_c for reactants/products in solution
- This is K_p for a reaction that has any gaseous reactants or products

\ln = logarithm to base e
= $\log_{10} \times 2.30259\dots$

Calculating Free Energy using Q

- $8\text{Fe(s)} + 6\text{NO}_2\text{(g)} \rightleftharpoons 4\text{Fe}_2\text{O}_3\text{(s)} + 3\text{N}_2\text{(g)}$
- $\Delta G^\ominus = -238.5 \text{ kJ mol}^{-1}$
- Let's say we have 10^6 Pa of N_2 and 10 Pa NO_2 in our reactor at 4500 K .

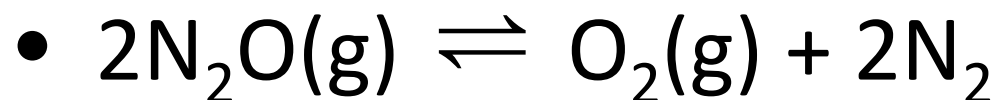
$$Q = \frac{(p_{\text{N}_2})^3}{(p_{\text{NO}_2})^6} = \frac{10^{18}}{10^6} = 10^{12}$$

- $\Delta G = \Delta G^\ominus + RT \ln Q$
 $= -238500 + (8.314 \times 4500 \ln(10^{12})) \text{ J mol}^{-1}$
 $= -238500 + 1034800 \text{ J mol}^{-1}$
 $= 796.3 \text{ kJ mol}^{-1}$

Worked Example 9.10*

- $2\text{N}_2\text{O}(\text{g}) \rightleftharpoons \text{O}_2(\text{g}) + 2\text{N}_2$ $T = 60^\circ\text{C}?$
- $\Delta S^\ominus = 148 \text{ JK}^{-1}\text{mol}^{-1}$
- $\Delta H^\ominus = -163.0 \text{ kJ mol}^{-1}$
- $\Delta G^\ominus = -163 \text{ kJ mol}^{-1} - 333 \text{ K} \times (148 \text{ JK}^{-1}\text{mol}^{-1})$
- $\Delta G^\ominus = -163 \text{ kJ mol}^{-1} - 49 \text{ kJmol}^{-1}$
- $\Delta G^\ominus = -212 \text{ kJ mol}^{-1}$
- $\Delta G^\ominus = -RT \ln K$
- $\ln K = -\Delta G^\ominus / RT = 212000 \text{ J mol}^{-1} / (8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 333 \text{ K})$
- $\ln K = 76.6$
- $K_p = e^{76.6}$

Worked Example 9.10*



$T = 60^\circ\text{C}?$

- $\Delta G^\ominus = -212 \text{ kJ mol}^{-1}$

- $\Delta G^\ominus = -RT \ln K$

- $\ln K = 76.6$

- $K_p = e^{76.6}$

- $K_p = 10^{76.6/2.303}$

- $K_p = 10^{33.26}$

- $K_p = 10^{0.26} \times 10^{33} = 1.8 \times 10^{33}$

I've shown you this so you can't
use the 'my calculator can't
handle numbers that big' excuse

How Systems at Equilibrium Respond to Change

- If an equilibrium is disturbed, the system will respond so as to restore the equilibrium.
- This is called **Le Châtelier's principle**
- e.g.:
 - If we add reactant X, some of it will react
 - If we take away product Y, the reaction will produce more of it
 - If we increase the temperature of an exothermic reaction, it will go backwards
 - If we increase the temperature of an endothermic reaction, it will go forwards

Le Châtelier's principle

- K for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is 0.106.
- If we start with 1 atm of dinitrogen tetroxide, we end up with 0.30 atm NO_2 and 0.85 atm N_2O_4 .
- Let's add another 1 atm NO_2 to the same volume: what happens?

$$Q_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{(1.3)^2}{0.85} = 1.99$$

$$K_p = 0.106$$

So we need to decrease p_{NO_2}
and increase $p_{\text{N}_2\text{O}_4}$.

$$0.090 + 0.053x = 1.69 - 2.6x + x^2 \quad K_p = 0.106 = \frac{(1.3 - x)^2}{0.85 + 0.5x}$$

$$x^2 - 2.653x + 1.6 = 0$$

$$x = 0.67$$

$$p_{\text{NO}_2} = 0.63 \text{ atm} \quad p_{\text{N}_2\text{O}_4} = 1.19 \text{ atm}$$

Changing the Pressure

- K for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is 0.106.
- We start with 1 atm N_2O_4 .
- Now, without adding anything, let's put these gases in a balloon and go to Mars, where atmospheric pressure is 0.6% of Earth, so $p = 0.006$ atm

$$K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{(2x)^2}{0.006 - x} = 0.106$$

$$6.36 \times 10^{-4} - 0.106x = 4x^2$$

$$x^2 + 0.0265x - 1.59 \times 10^{-4} = 0$$

$$x = 5.04 \times 10^{-3}$$

$$p_{\text{NO}_2} = 0.0108 \text{ atm}$$

$$p_{\text{N}_2\text{O}_4} = 0.0010 \text{ atm}$$

Changing the Temperature

$$1) \Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$2) \ln K = -\Delta G^{\ominus}/RT$$

$$\text{So: } \ln K = -\Delta H^{\ominus}/RT + \Delta S^{\ominus}/R$$

We want to know how $\ln K$ changes with T , so we take the derivative:

$$d(\ln K)/dT = \Delta H^{\ominus}/RT^2$$

This is called the **van't Hoff equation**



See, calculus is another thing you're not allowed to forget!

Changing the Temperature

- $\ln K_1 = -\Delta H^\ominus / RT_1 + \Delta S^\ominus / R$
 - $\ln K_2 = -\Delta H^\ominus / RT_2 + \Delta S^\ominus / R$
- Actually, let's ignore calculus!

So:

- $\ln K_1 - \ln K_2 = -\Delta H^\ominus / RT_1 + \Delta S^\ominus / R - (-\Delta H^\ominus / RT_2 + \Delta S^\ominus / R)$
- $\ln K_1 - \ln K_2 = -\Delta H^\ominus / RT_1 + \Delta H^\ominus / RT_2$

$$\ln K_1 - \ln K_2 = \Delta H^\ominus / R (1/T_2 - 1/T_1)$$

Changing the Temperature



- $K = 64$ at 390°C

- What is K at 10°C ?

	$\Delta H_f^\ominus (\text{kJmol}^{-1})$	
$\text{H}_2(\text{g})$	0	$\ln K_1 - \ln K_2 = \Delta H^\ominus / R (1/T_2 - 1/T_1)$
$\text{I}_2(\text{g})$	62.4	$\ln K_1 - \ln(64) = -9200/8.314(1/663 - 1/283)$
$\text{HI}(\text{g})$	26.6	$\ln K_1 = -1107(-0.00215) + \ln(64)$
		$\ln K_1 = 2.38 + 4.16$

$$K_1 = e^{6.54} = 692$$

$$\Delta H^\ominus = 53.2 - 62.4 = -9.2 \text{ kJmol}^{-1}$$

Exothermic : should be **more favoured** at low temperature

Equilibria and Carbon Dioxide Sequestration

- I am interested in preventing calcium carbonate from forming
- There are a lot of equilibria to worry about
- e.g., $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$
- What should K be for this at 25 °C?

	ΔG_f^\ominus (kJmol ⁻¹)	$\ln K = -\Delta G^\ominus / RT$
$\text{H}_2\text{CO}_3(\text{aq})$	-623.08	$\ln K = -100 \text{ J mol}^{-1} / (8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K})$
$\text{H}_2\text{O}(\text{l})$	-237.2	$\ln K = -0.04$
$\text{CO}_2(\text{aq})$	-385.98	$K = 0.96$

$$\Delta G^\ominus = 0.10 \text{ kJmol}^{-1}$$

But, all the references I have found have it between 0.01 and 0.001

Equilibria and Carbon Dioxide Sequestration

- The real world data might be confused by all those other equilibria we saw at the beginning of chapter
- The numbers in the textbook are derived from lots of different systems and have associated errors
- The numbers in the textbook might just be bogus
- Take home message: **Do not invest your fortune in a carbon dioxide sequestration plant based only on calculations done using numbers in this textbook**

Things you ought to know

- Thermodynamic definitions (system, surroundings, heat, work, etc.): $U = q + w$
- Heat capacity and specific heat: $q = mc\Delta T$
- Enthalpy: $H = q$ for a system at constant p
- Entropy: $S = q/T$, $S = k_B \ln W$
- Gibbs Energy Change: $\Delta G = \Delta H - T\Delta S$
- Standard Enthalpy, Entropy, Gibbs Energy: H^\ominus , S^\ominus , G^\ominus
- Enthalpy, Entropy, Gibbs Energy of formation: H_f^\ominus , S_f^\ominus , G_f^\ominus
- Hess's Law and Equivalents:

$$\Delta H^\ominus = \sum \Delta H_f^\ominus \text{products} - \sum \Delta H_f^\ominus \text{reactants}$$

$$\Delta S^\ominus = \sum S_f^\ominus \text{products} - \sum S_f^\ominus \text{reactants}$$

$$\Delta G^\ominus = \sum \Delta G_f^\ominus \text{products} - \sum \Delta G_f^\ominus \text{reactants}$$

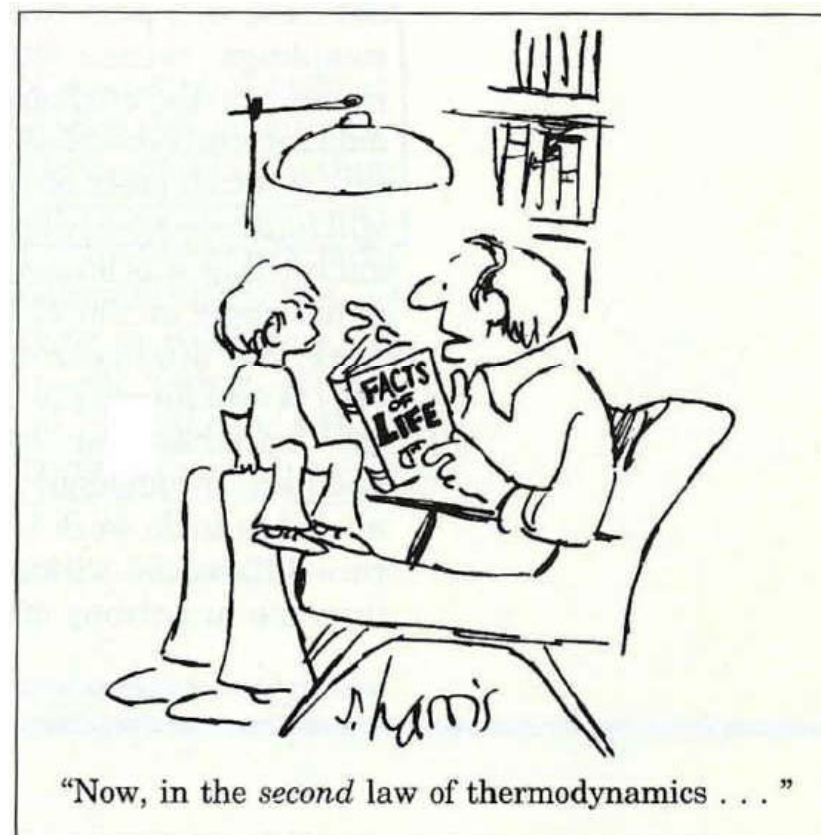
- Bond enthalpies

$$\Delta H^\ominus = \sum H_{\text{bond}} \text{reactants} - \sum H_{\text{bond}} \text{products}$$

Things you ought to know

- The Second Law of Thermodynamics

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$



Things you ought to know

- The equilibrium constant, K
- The reaction quotient, Q
- $\Delta G = \Delta G^\ominus + RT \ln Q$
- $\Delta G^\ominus = RT \ln K$
- ...

$$Q_p = \frac{\left(\frac{p_C}{p^\ominus}\right)^c \left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a \left(\frac{p_B}{p^\ominus}\right)^b}$$

$$Q_c = \frac{\left(\frac{[C]}{c^\ominus}\right)^c \left(\frac{[D]}{c^\ominus}\right)^d}{\left(\frac{[A]}{c^\ominus}\right)^a \left(\frac{[B]}{c^\ominus}\right)^b}$$

$$K_p = \frac{\left(\frac{p_C}{p^\ominus}\right)^c \left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a \left(\frac{p_B}{p^\ominus}\right)^b}$$

$$K_c = \frac{\left(\frac{[C]}{c^\ominus}\right)^c \left(\frac{[D]}{c^\ominus}\right)^d}{\left(\frac{[A]}{c^\ominus}\right)^a \left(\frac{[B]}{c^\ominus}\right)^b}$$

Except I won't ask you any questions
about converting K_c to K_p or vice versa

Nothing is true.
Everything is examinable.

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