

Chemistry 2000 Slide Set 12:
Temperature dependence of the
equilibrium constant

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Temperature dependence of the equilibrium constant

- So far, all the problems we have solved have been at 25°C because our tables of free energies of formation are at this temperature.
- ΔH and ΔS vary relatively slowly with temperature. However, $\Delta G = \Delta H - T\Delta S$ has a strong dependence on T .
- At any temperature, $\Delta_r G_m^\circ(T) = -RT \ln K(T)$.
- Suppose we have two temperatures, T_1 and T_2 . Let $K_1 = K(T_1)$ and $K_2 = K(T_2)$.
Then

$$\Delta_r G_m^\circ(T_1) = \Delta_r H_m^\circ - T_1 \Delta_r S_m^\circ = -RT_1 \ln K_1$$

$$\Delta_r G_m^\circ(T_2) = \Delta_r H_m^\circ - T_2 \Delta_r S_m^\circ = -RT_2 \ln K_2$$

$$\Delta_r H_m^\circ - T_1 \Delta_r S_m^\circ = -RT_1 \ln K_1$$

$$\Delta_r H_m^\circ - T_2 \Delta_r S_m^\circ = -RT_2 \ln K_2$$

- Divide both sides by RT :

$$\frac{\Delta_r H_m^\circ}{RT_1} - \frac{\Delta_r S_m^\circ}{R} = -\ln K_1$$

$$\frac{\Delta_r H_m^\circ}{RT_2} - \frac{\Delta_r S_m^\circ}{R} = -\ln K_2$$

- If we assume that $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ are independent of temperature and subtract the two equations, we get

$$\frac{\Delta_r H_m^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \ln K_2 - \ln K_1$$

or

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta_r H_m^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Exponentials and logarithms

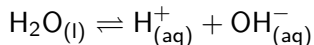
- $\ln e^x = x$

- $e^{\ln x} = x$

⇒ the exponential function and the natural logarithm are inverse functions.

Example: Temperature dependence of K_w

- K_w is the equilibrium constant for the autodissociation of water:



- $K_w = 1.01 \times 10^{-14}$ at 25°C and $\Delta_r H^\circ = 55.8 \text{ kJ mol}^{-1}$.
- What is K_w at 37°C ?

Answer: 2.4×10^{-14}

- For neutral water, $a_{\text{H}^+} = a_{\text{OH}^-}$ so

$$K_w = (a_{\text{H}^+})(a_{\text{OH}^-}) = (a_{\text{H}^+})^2$$
$$\therefore a_{\text{H}^+} = \sqrt{K_w}$$

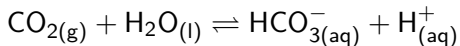
- At 37°C,

$$a_{\text{H}^+} = \sqrt{2.4 \times 10^{-14}} = 1.5 \times 10^{-7}$$
$$\therefore \text{pH} = -\log_{10}(1.5 \times 10^{-7}) = 6.81$$

- The pH of neutral water is 7 only at 25°C!
- Similarly, the rule $\text{pOH} = 14 - \text{pH}$ only applies at 25°C.

Effect of temperature on reaction of CO₂ with water

- For the reaction



	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{CO}_{2(\text{g})}$	-393.5
$\text{HCO}_{3(\text{aq})}^-$	-691.11
$\text{H}_2\text{O}_{(\text{l})}$	-285.840

- We previously calculated $K = 1.47 \times 10^{-8}$ at 25 °C for this reaction.
- The average surface temperature of the sea is 16.1 °C.
- Calculate
 - $\Delta_r H^\circ$
 - K at 16.1 °C

Effect of temperature on reaction of CO₂ with water

(continued)

- Answers:
 - $\Delta_r H^\circ = -11.8 \text{ kJ mol}^{-1}$
 - $K = 1.70 \times 10^{-8}$ at 16.1 °C
- Note that the increase in K with decreasing temperature is consistent with Le Chatelier's principle.

Boiling point as a function of pressure

- A liquid boils when its vapor pressure equals the atmospheric pressure.

The **normal boiling point** is the boiling point at 1 atm pressure.

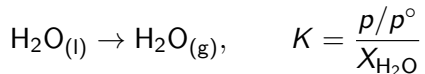
$$1 \text{ atm} = 1.013 25 \text{ bar}$$

- Lethbridge is about 940 m above sea level.
The atmospheric pressure here is about 90 kPa on a typical day.
- What is the boiling point of water in Lethbridge?

Answer: 96.7 °C

Boiling-point elevation

- What effect does a solute have on the boiling point of a solvent?
- Again consider



$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta_{\text{vap}} H_m^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- Take $T_1 =$ boiling point of pure solvent, $K_1 = p/p^\circ$, and note that $\Delta_{\text{vap}} H_m^\circ > 0$.
- Since $X_{\text{H}_2\text{O}} < 1$ for a solution, $K_2 > K_1$.

- If $K_2 > K_1$, then in the formula

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta_{\text{vap}} H_m^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

the left-hand side is positive, which means that

$$\frac{1}{T_1} - \frac{1}{T_2} > 0$$

(since $\Delta_{\text{vap}} H_m^\circ > 0$), or

$$T_1 < T_2$$

- The boiling point of a solution is higher than the boiling point of the pure solvent.

Example: What is the boiling point of a solution made by dissolving 0.5032 mol NaCl in 1.01 kg of water at (exactly) 1 atm pressure?

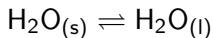
Data: The enthalpy of vaporization of water at the normal boiling point is 40.66 kJ/mol.

Note: This is roughly the salt concentration you would use to boil pasta.

Answer: 100.51 °C

Freezing-point depression

- What effect does a solute have on the freezing point of a solvent?
- The process is



with

$$K = \frac{a_l}{a_s} = \frac{X_{\text{H}_2\text{O}}}{1}$$

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta_{\text{fus}} H_m^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- Take $T_1 =$ freezing point of pure solvent, $K_1 = 1$, and note that $\Delta_{\text{fus}} H_m^\circ > 0$.
- Since $X_{\text{H}_2\text{O}} < 1$ for a solution, $K_2 < K_1 = 1$.

- If $K_2 < K_1$, then in the formula

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta_{\text{fus}} H_m^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

the left-hand side is negative, which means that

$$\frac{1}{T_1} - \frac{1}{T_2} < 0$$

(since $\Delta_{\text{fus}} H_m^\circ > 0$), or

$$T_1 > T_2$$

- The freezing point of a solution is lower than the freezing point of the pure solvent.

Example: What is the freezing point of a solution made by dissolving 100 g of sucrose ($C_{12}H_{22}O_{11}$) in 500 g of water?

Data: The enthalpy of fusion of ice at the normal freezing point is 6007 J/mol.

Answer: $-1.08^{\circ}C$