## CHEMISTRY 203

# Thermodynamics of the Dissolution of Borax

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## Purpose

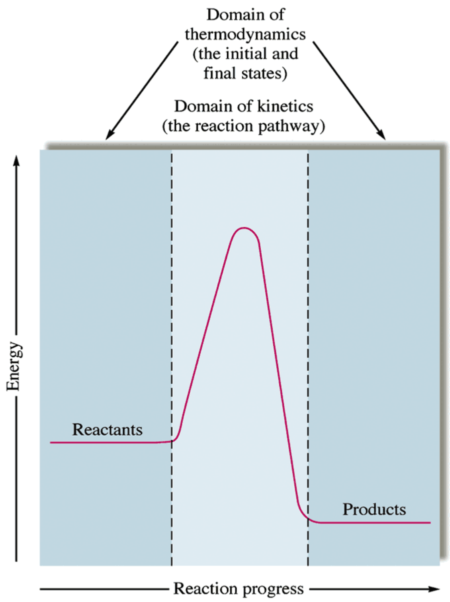
1. To learn about the laws of **thermodynamics**.
2. To determine the tetraborate concentration at different temperatures by titration against standardized HCl .
3. To determine the solubility product of borax as a function of temperature.
4. To determine the **standard free energy change (ΔG°), the standard enthalpy change (ΔH°), and the standard entropy change (ΔS°)** for the dissolution of borax in an aqueous solution.

## Theoretical Background

***Kinetics***: The rate of a reaction depends on the pathway from reactants to products; this is the domain of kinetics.

***Thermodynamics***: tells us whether a reaction is spontaneous based only on the properties of the reactants and products.

Diamond → Graphite
Spontaneous but Slow



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# Thermodynamic Functions

- Entropy
- Enthalpy
- Free Energy (Gibbs Free Energy)

And their relationship to Spontaneity of a chemical reaction

# Entropy and the 2nd Law of Thermodynamics

**1st Law:** Law of conservation of energy, the energy of the universe is constant, the various forms of energy can be interchanged in physical and chemical processes.

**2nd Law:** predict whether a final state is accessible from an initial state spontaneously.

***In any spontaneous process, there is always an increase in the entropy of the universe.***

$$\Delta S_{univ} > 0$$

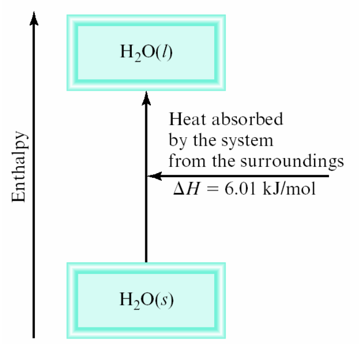
# Spontaneous Processes and Entropy

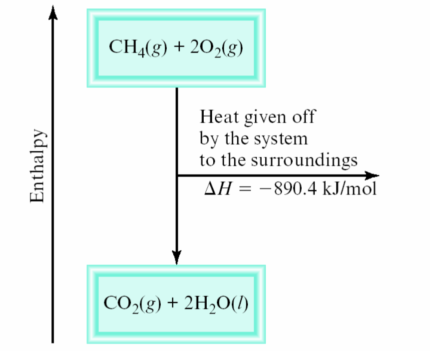
- Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.
- A spontaneous process is one that occurs without outside intervention.
- The driving force for a spontaneous process is an increase in the entropy of the universe.
- Entropy, $S$, can be viewed as a measure of randomness, or disorder.

***Enthalpy (H)*** is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

$$\Delta H = H\,(\text{products}) - H\,(\text{reactants})$$

$\Delta H$ = heat ***given off*** or ***absorbed*** during a reaction **at constant pressure**





$H_{\text{products}} > H_{\text{reactants}}$

$\Delta H > 0$ ***Endothermic process***

$H_{\text{products}} < H_{\text{reactants}}$

$\Delta H < 0$ ***Exothermic process***

# Standard Free Energy

The ***standard free-energy of reaction ($\Delta G^0_{\text{rxn}}$)*** is the free-energy change for a reaction when it occurs under standard-state conditions.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G^0_{\text{rxn}} = [c\Delta G^0_f(C) + d\Delta G^0_f(D)] - [a\Delta G^0_f(A) + b\Delta G^0_f(B)]$$

$$\Delta G^0_{\text{rxn}} = \Sigma n\Delta G^0_f(\text{products}) - \Sigma m\Delta G^0_f(\text{reactants})$$

***Standard free energy of formation*** ($\Delta G^0_f$) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

$\Delta G^0_f$ of any element in its stable form is zero.

## Free Energy and Spontaneity

$\Delta G = \Delta H - T\Delta S$ (from the standpoint of the system)

- A process (at constant $T$, $P$) is spontaneous in the direction in which free energy decreases:

$$-\Delta G \textit{ means } +\Delta S_{\text{univ}}$$

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Spontaneous process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Equilibrium process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

***Gibbs free energy (G)***

For a constant temperature and constant pressure process:

$\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

$\Delta G < 0$ The reaction is spontaneous in the forward direction.

$\Delta G > 0$ The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$ The reaction is at equilibrium.

# Effect of ΔH and ΔS on Spontaneity

| $\Delta H$ | $\Delta S$ | Result |
|---|---|---|
| – | + | spontaneous at all temps |
| + | + | spontaneous at high temps |
| – | – | spontaneous at low temps |
| + | – | not spontaneous at any temp |

# Free Energy and Chemical Equilibrium

$$\Delta G = \Delta G^0 + RT \ln Q$$

$R$ is the gas constant (8.314 J/K•mol)

$T$ is the absolute temperature (K)

$Q$ is the reaction quotient

At Equilibrium $\Delta G = 0$ $Q = K$

$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = -RT \ln K$$

# Temperature Dependence of K

$$\Delta G^0 = -RT \ln K \qquad \Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G° = -RT \ln(K) = \Delta H° - T\,\Delta S°$$

$$\ln(K) = -\frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$$

- $y = mx + b$
- ($\Delta H°$ and $S°$ ≈ independent of temperature over a small temperature range)

# Dissolution of Borax

**Borax**, sodium tetraborate octahydrate, is a slightly soluble salt which acts as a weak base in water. "Borax" is a naturally occurring compound; it is in fact the most important source of the element boron, and it has been used for many years as a water softening agent.

$$Na_2B_4O_5(OH)_4 \cdot 8\,H_2O_{(s)} \rightarrow 2\,Na^+_{(aq)} + B_4O_5(OH)_4^{2-}{}_{(aq)} + 8\,H_2O_{(l)}$$

The K expression for this reaction is: $K = [Na^+]^2[\,B_4O_5(OH)_4{}^{2-}]$

Note that the borax solvation reaction equilibrium constant is the solubility product Ksp for borax:

$$K = Ksp = [Na^+]^2[\,B_4O_5(OH)_4{}^{2-}]$$

By the stoichiometry of the reaction $[Na^+] = 2\,[\,B_4O_5(OH)_4{}^{2-}]$

=> $Ksp = [(2\,[\,B_4O_5(OH)_4{}^{2-}])\,]^2\,[\,B_4O_5(OH)_4{}^{2-}]$

$$Ksp = 4\,[\,B_4O_5(OH)_4{}^{2-}]^3$$

**Determination of Ksp** by analysis of a saturated solution of borax.

Tetraborate (weak base) is titrated with a strong acid:

$B_4O_5(OH)_4^{2-}{}_{(aq)} + 2\,H^+{}_{(aq)} + H_2O_{(l)} \rightarrow 4\,H_3BO_3{}_{(aq)}$

Therefore, calculate

- the number of moles of tetraborate,
- the number of moles of sodium ion,
- the molar concentrations of the two ions and,
- the value of Ksp.

Repeat at different Temperatures

**Method 1:** Plot ln Ksp versus 1/T

**Determine ΔH⁰ and ΔS⁰** from slope and intercept

$$\ln K = \ln \mathrm{Ksp} = -\frac{\Delta \mathrm{H}^\circ}{\mathrm{R}}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

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## Method 2:

After determination of Ksp at two different temperatures, calculate **ΔH⁰** from

$$\ln \frac{\mathrm{Ksp}_1}{\mathrm{Ksp}_2} = \frac{\Delta \mathrm{H}^\circ}{\mathrm{R}}\left(\frac{1}{\mathrm{T}_2} - \frac{1}{\mathrm{T}_1}\right)$$

Knowing **ΔG°** at each temperature from $\Delta G^\circ = -RT \ln K$

**ΔS°** can be calculated from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

The literature values for **enthalpy** and **entropy** of the dissolution of **borax** in water are 110 kJ/mol and 380 J/K.mol, respectively.