

Announcements

To join clicker to class today (Clickers with LCD display joins automatically):

- Turn on the Clicker (the red LED comes on).
- Push “Join” button followed by “20” followed by the “Send” button (switches to flashing green LED if successful).

- Now hiring students to prep for general chemistry next Fall. See Ms. Hauer in HS-449

- Even if the weather is nice do not forget to wear appropriate clothing to lab! Calorimetry lab involves caustics that will eat your skin!
- Exam scores may be delayed as a computer error requires scoring by hand.
- Quiz tomorrow on ΔH .

Review

- ΔH_f° to calculate ΔH_{RXN}
 - Key relationship: $\Delta H_{\text{RXN}}^\circ = \sum \Delta H_f^\circ(\text{prod}) - \sum \Delta H_f^\circ(\text{react})$
- Fuel Values:
 - kJ/g
 - kJ/mL
 - CO₂ intensity (mol/kJ)
- Hess's Law: $\Delta H(\text{A} \rightarrow \text{C}) = \Delta H(\text{A} \rightarrow \text{B}) + \Delta H(\text{B} \rightarrow \text{C})$

Entropy & Free Energy

- Enthalpies of Solution ($\Delta H_{\text{sol'n}}$, ΔH_{ionic} , $\Delta H_{\text{H-bonds}}$, $\Delta H_{\text{ion-dipole}}$)
- Entropy (S , ΔS , spontaneity)
- Free Energy (ΔG , spontaneity)

Contributions to $\Delta H_{\text{sol'n}}$ of NaCl

Process of dissolving salt	Label	ΔH
1) Ionic crystal lattice to separate solvated ions	ΔH_{ionic}	> 0
2) Breaking H-bonds	$\Delta H_{\text{H-bond}}$	> 0
3) Water reorganizes to solvate ions	$\Delta H_{\text{ion-dipole}}$	< 0
Sum	$\Delta H_{\text{sol'n}}$	> 0

Entropy versus Temperature and Phase

Chang Fig. 18.6

Second Law of Thermodynamics

- A process is spontaneous only if the entropy of the universe increases during the process.
- Entropy is times arrow, as time moves forward entropy increases.
- Spontaneous Process: $\Delta S_{\text{univ}} > 0$
- Non-spontaneous Process $\Delta S_{\text{univ}} < 0$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$.
- $\Delta S_{\text{sys}} \approx \Delta S^{\circ}_{\text{rxn}} = \sum S^{\circ}_{\text{prod}} - \sum S^{\circ}_{\text{reac}}$
 - $S(\text{perfect crystal at } 0 \text{ K}) = 0$
 - S° is relative to this perfect crystal

Possible combinations of ΔS_{sys} and ΔS_{surr}

- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T$
 - $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$, because $\Delta H < 0$ heats surroundings
 - $1/T$ factor because at high T same ΔH (q) causes less fractional change in entropy (disorder).
- $\Delta H < 0$, $\Delta S_{\text{sys}} > 0$ $\Delta S_{\text{univ}} > 0$ always spontaneous
- $\Delta H < 0$, $\Delta S_{\text{sys}} < 0$ $\Delta S_{\text{univ}} = ?$ spontaneous at low T
- $\Delta H > 0$, $\Delta S_{\text{sys}} < 0$ $\Delta S_{\text{univ}} < 0$ never spontaneous
- $\Delta H > 0$, $\Delta S_{\text{sys}} > 0$ $\Delta S_{\text{univ}} = ?$ spontaneous at high T

ΔG – Free Energy

- $\Delta G_{\text{sys}} = -T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$
- Usually drop "sys" subscripts: $\Delta G = \Delta H - T\Delta S$
- Interpretation of G:
 - $\Delta G < 0$ spontaneous
 - $\Delta G > 0$ nonspontaneous
 - $\Delta G = 0$ equilibrium

Calculating ΔG

- From ΔH_f° and S°

– Calculate ΔH° and ΔS° , then use in $\Delta G = \Delta H - T\Delta S$

– Ex: $\text{NaCl(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O(l)}$

$S^\circ(\text{J}\cdot\text{mol}^{-1}\text{K}^{-1})$	72.1	70.0	59.0	56.5	70.0
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$\Delta H_f^\circ(\text{kJ}\cdot\text{mol}^{-1})$	-411.2	-285.8	-240.1	-167.2	-285.8
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$$\Delta S_{\text{rxn}}^\circ = 43.4 \text{ J/K}$$

$$\Delta H_{\text{rxn}}^\circ = 3.9 \text{ kJ}$$

$$\Delta G_{\text{rxn}}^\circ = 3.9 \times 10^3 \text{ J} - (298 \text{ K})(43.4 \text{ J/K}) = -9.0 \times 10^3 \text{ J}$$