

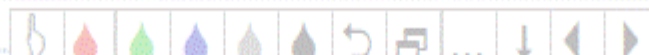
Announcements – Lecture XX – Thursday, Apr 12th

1. iClicker:



Pick any letter a-e

2. No Class: Tuesday, April 17th – Academic Monday



19.1 Entropy

A Review of Terminology



SYSTEM: What we are interested in ...
the chemical reaction.

SURROUNDINGS: Everything else.

UNIVERSE = SYSTEM + SURROUNDINGS

Chem III: Heat Transfer (Enthalpy) in the system.

$$\Delta H_{\text{RXN}}^{\circ} = \sum \Delta H_{\text{f}}^{\circ} (\text{products}) - \sum \Delta H_{\text{f}}^{\circ} (\text{reactants})$$

$$\Delta H_{\text{RXN}}^{\circ} < 0 : \text{Exothermic}$$

$$\Delta H_{\text{RXN}}^{\circ} > 0 : \text{Endothermic}$$

19.1 Entropy

Spontaneous Process V Nonspontaneous Process



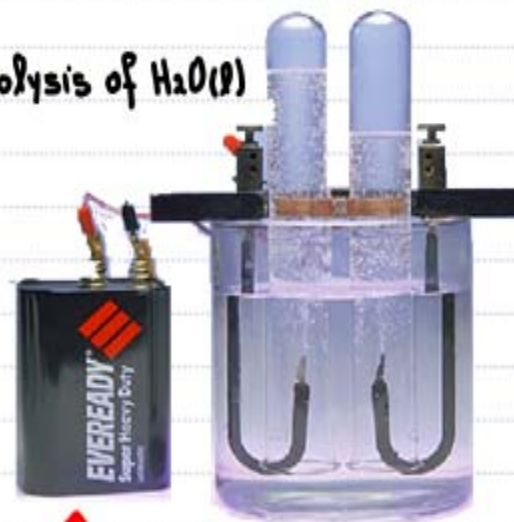
Butane burner

SPONTANEOUS:

Any process that is able to occur without being continuously driven by an external source of energy

- May require an initial input of energy to overcome E_0 to get it started.

Electrolysis of $H_2O(l)$



Requires a continuously external energy source.

Nonspontaneous

19.1 Entropy

Enthalpy a Measure of Spontaneity?

Nonspontaneous



$$\begin{aligned}\Delta H_{\text{RXN}}^{\circ} &= 2\Delta H_f^{\circ} \text{H}_2(g) + \Delta H_f^{\circ} \text{O}_2(g) - 2\Delta H_f^{\circ} \text{H}_2\text{O}(l) \\ &= 2(0) + 0 - 2(-285.8) \\ &= 571.6 \text{ kJ} \\ &\text{Endothermic}\end{aligned}$$

Spontaneous



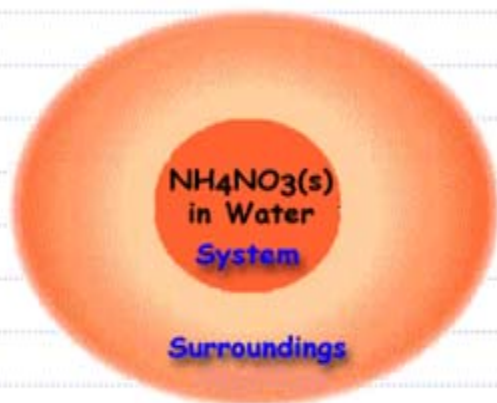
$$\begin{aligned}\Delta H_{\text{RXN}}^{\circ} &= 8\Delta H_f^{\circ} \text{CO}_2(g) + 10\Delta H_f^{\circ} \text{H}_2\text{O}(g) - 2\Delta H_f^{\circ} \text{C}_4\text{H}_{10}(g) - 13\Delta H_f^{\circ} \text{O}_2(g) \\ &= 8(-393.5) + 10(-241.8) - 2(-125.6) - 13(0) \\ &= -5,314.6 \text{ kJ} \\ &\text{Exothermic}\end{aligned}$$



$$\begin{aligned}\Delta H_{\text{RXN}}^{\circ} &= \Delta H_f^{\circ} \text{H}_2\text{O}(g) - \Delta H_f^{\circ} \text{H}_2\text{O}(l) \\ &= -241.8 - (-285.8) \\ &= 44 \text{ kJ} \\ &\text{Endothermic} \text{ ☹️}\end{aligned}$$

19.1 Entropy

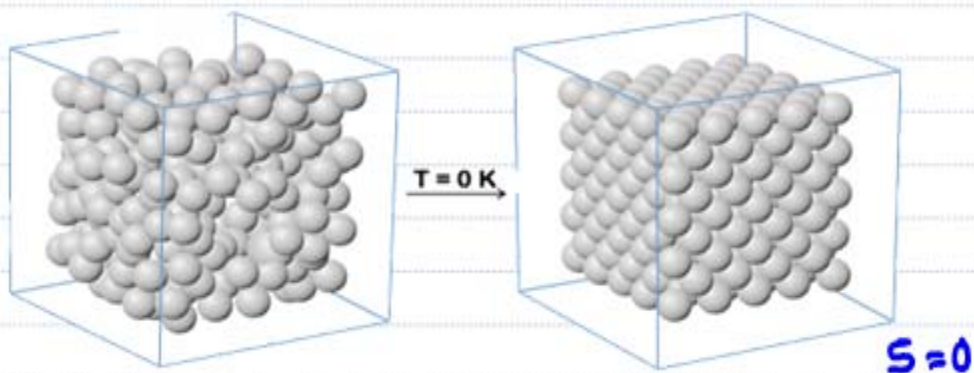
Entropy a Measure of Spontaneity?



ENTROPY (S): A measure of disorder and the natural tendency to disorder.

SPONTANEOUS PROCESS: $\Delta S_{\text{UNIVERSE}} > 0$

$$\Delta S_{\text{UNIVERSE}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}} > 0$$



3RD LAW OF THERMODYNAMICS:

The entropy of a pure crystalline system is ϕ @ absolute zero.



19.1 Entropy

Trends in Entropy

▶ $S^\circ(\text{gases}) \gg S^\circ(\text{liquids}) > S^\circ(\text{solids})$.

Self explanatory.

▶ The entropy of a substance increases with temperature.

Increase in T increases vibrations and thus entropy.

▶ The more complex the molecule, the greater the value of S° .

The larger the molecule the greater the entropy.

▶ Entropies of ionic solids depend on coulombic attractions.

The lesser the force of attraction the greater the entropy: $\text{Na}^+, \text{Cl}^- > \text{Ca}^{2+}, \text{O}^{2-}$.

▶ Entropy usually increases when a pure liquid or solid dissolves in a solvent.

Dissolving salts or pure liquids in a solvent increases the entropy.



19.1 Entropy

Trends in Entropy

Which of the following would you expect to have the **highest** entropy?

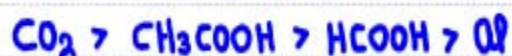
- a) $\text{CO}_2(\text{g})$ ✓ b) $\text{Al}(\text{s})$
c) $\text{CH}_3\text{COOH}(\text{l})$ d) $\text{HCOOH}(\text{l})$



CO_2 is in the gas phase.

$\text{CH}_3\text{COOH} > \text{HCOOH}$, both are liquids but CH_3COOH has a greater molar mass (is bigger) than HCOOH .

Al would have the lowest entropy since it is a solid.



Which of the following would you expect to have the **smallest** entropy?

- a) $\text{KBr}(\text{s})$ b) $\text{MgO}(\text{s})$ ✓
c) $\text{NaCl}(\text{s})$ d) $\text{NaF}(\text{s})$



All are solids so we are looking for the one with the strongest force of attraction.

First looking at the magnitude of the charge: MgO

The 3 left all have +1, -1, charge. So now we are looking at the size of the ions involved. The smaller the ion the greater the force of attraction.




19.2 Calculating Entropy Change

Standard Entropy Change for a Phase Change

$$\Delta S_{\text{phase change}} = \frac{\Delta H_{\text{PHASE CHANGE}}}{T_{\text{PHASE CHANGE}}}$$

Calculate the entropy change when 3.48 moles of ether condenses at its boiling point of 34.6 °C.

ΔH_{vap} of Ether = 26.5 kJ.mol⁻¹

 $\Delta S = ?00 \text{ J/K}$

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Condensation: g → l

$$\Delta S = S_{\text{liquid}} - S_{\text{gas}}$$

∴ expect $\Delta S < 0$

$$\begin{aligned}\Delta S_{\text{condense}} &= - \frac{\Delta H_{\text{vap}}}{T(\text{K})} \\ &= - \frac{3.48(26,500)}{307.6} \\ &= - 300 \text{ J/K}\end{aligned}$$

19.2 Calculating Entropy Change

Entropy Change in the Surroundings

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{SYS}} + \Delta S_{\text{SURR}}$$

$$\Delta S^{\circ}_{\text{RXN}} = \sum S^{\circ}(\text{PRODUCTS}) - \sum S^{\circ}(\text{REACTANTS})$$

$$\Delta S_{\text{SURR}} = -\frac{q_{\text{SYS}}}{T}, \text{ @ constant pressure}$$

$$q_{\text{SYS}} = \Delta H_{\text{RXN}}$$

$$\Delta S_{\text{SURR}} = -\frac{\Delta H_{\text{RXN}}}{T}$$

$$\Delta S^{\circ}_{\text{UNIV}} = \Delta S^{\circ}_{\text{RXN}} - \frac{\Delta H^{\circ}_{\text{RXN}}}{T}$$

For a spontaneous process, $\Delta S_{\text{univ}} > 0$, and the reaction is thus product favored.

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{RXN}} - \frac{\Delta H_{\text{RXN}}}{T}$$

Battle !!

	↓	Entropy	vs	↓	Enthalpy	
Battle !!	{	$\Delta S > 0$		$\Delta H > 0$	Endothermic	
		$\Delta S < 0$		$\Delta H < 0$	Exothermic	

No Battle

No Battle	1* 2*	{	$\Delta S > 0$	$\Delta H < 0$	Exothermic
			$\Delta S < 0$	$\Delta H > 0$	Endothermic

1*: ΔS_{univ} always > 0 , product favored.
 2*: ΔS_{univ} always < 0 , reactant favored