

## 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



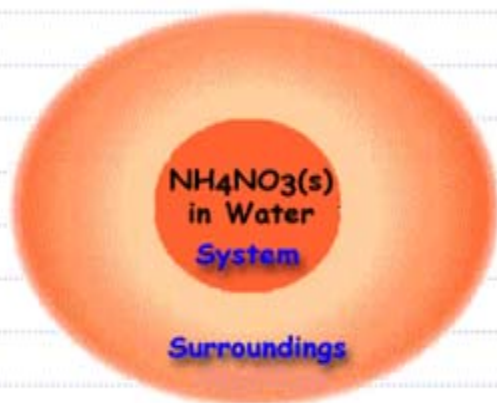
$$\begin{aligned}\Delta H_{\text{RXN}}^{\circ} &= 8\Delta H_f^{\circ} \text{CO}_2(g) + 10\Delta H_f^{\circ} \text{H}_2\text{O}(g) - 2\Delta H_f^{\circ} \text{C}_4\text{H}_{10}(g) - 13\Delta H_f^{\circ} \text{O}_2(g) \\ &= 8(-393.5) + 10(-241.8) - 2(-125.6) - 13(0) \\ &= -5,314.6 \text{ kJ} \\ &\text{Exothermic}\end{aligned}$$



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

## 19.1 Entropy

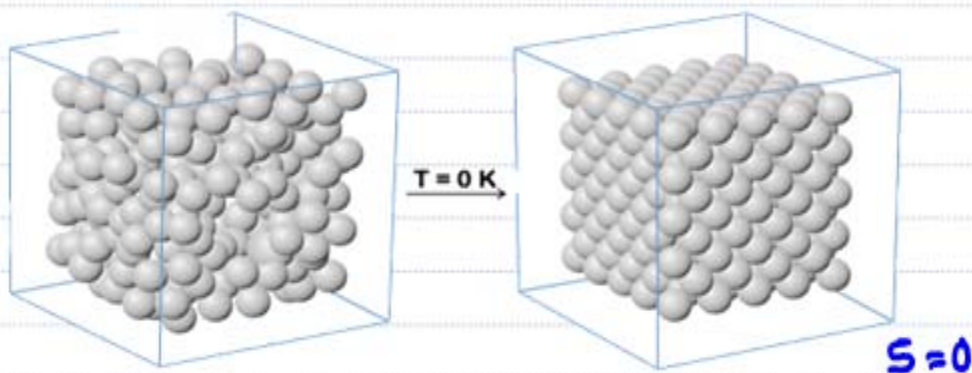
### Entropy a Measure of Spontaneity?



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

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

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



**3<sup>RD</sup> LAW OF THERMODYNAMICS:**

The entropy of a pure crystalline system is  $\phi$  @ 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  $S^\circ$ .

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)  $\text{HCOOH}(\text{l})$



$\text{CO}_2$  is in the gas phase.

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

$\text{Al}$  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:  $\text{MgO}$

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.

$\Delta H_{\text{vap}}$  of Ether = 26.5 kJ.mol<sup>-1</sup>

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

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

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\*:  $\Delta S_{\text{univ}}$  always  $> 0$ , product favored.  
 2\*:  $\Delta S_{\text{univ}}$  always  $< 0$ , reactant favored