

## Announcements – Lecture XXI – Thursday, Apr 19<sup>th</sup>

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1. iClicker:



Pick any letter a-e

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2. Quiz 9: Due Tuesday, April 24<sup>th</sup>.

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3. Owl: **All remaining Owls for Exam III are now up.** The due dates for some are different, based on projected coverage. *Just wanted to give you a heads up on the remaining Owls in this course as we quickly approach the end of the semester.*

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## 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

## 19.2 Calculating Entropy Change

### Entropy Change in the Surroundings

Consider the reaction  $\text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) = 2\text{NO}(\text{g}) + 2\text{H}_2(\text{g})$   
for which  $\Delta H^\circ = 752.2 \text{ kJ}$  and  $\Delta S^\circ = 351.6 \text{ J/K}$  at  $298.15 \text{ K}$

- At  $298.15 \text{ K}$  is this reaction product or reactant favored?
- Is the answer to a) entropy or enthalpy driven?

$$\Delta S^\circ_{\text{UNIV}} = \Delta S^\circ_{\text{SYS}} + \Delta S^\circ_{\text{SURR}}$$

$$\Delta S^\circ_{\text{SYS}} = \Delta S^\circ_{\text{RXN}} = 351.6 \text{ J/K}$$

$$\begin{aligned}\Delta S^\circ_{\text{SURR}} &= -\frac{\Delta H^\circ_{\text{RXN}}}{T} \\ &= -\frac{752,200 \text{ J}}{298.15 \text{ K}} = -2522.8 \text{ J/K}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{\text{UNIV}} &= 351.6 - 2522.8 \\ &= -2171.2 \text{ J/K}\end{aligned}$$

a)  $\Delta S^\circ_{\text{UNIV}} < 0$   
Nonspontaneous, reactant favored.

b)  $\Delta S^\circ_{\text{SYS}} > 0$   
 $\Delta S^\circ_{\text{SURR}} < 0$  ... determined by  $\Delta H^\circ$   
Thus  $\Delta S^\circ_{\text{UNIV}} < 0$  is enthalpy driven.

**NOTE:** To reduce the impact of  $\Delta S^\circ_{\text{SURR}}$ , then move away from standard temperature condition. Substantially increasing  $T$  would increase the effect of  $\Delta S^\circ_{\text{SURR}}$  and one could find a  $T$  in which  $\Delta S^\circ_{\text{SURR}}$  becomes  $> 0$ .  
This leads us to **GIBBS FREE ENERGY**.



## 19.3 Gibbs Free Energy

### Gibbs Free Energy and Spontaneity

$$G = H - TS \quad G = \text{Gibbs Free Energy}$$
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad \text{for a spontaneous reaction.}$$

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$
$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$
$$\underbrace{-T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}}_{\Delta G_{\text{sys}}} < 0$$

$\Delta G_{\text{sys}} < 0$  for a spontaneous reaction.

Gibbs Free Energy = the maximum work we can get from a reaction.

$\Delta G < 0$ : spontaneous in the forward direction.

$\Delta G > 0$ : nonspontaneous in the forward direction ... conversely spontaneous in the reverse direction.

$\Delta G = 0$ : at equilibrium

## 19.3 Gibbs Free Energy

### Standard Gibbs Free Energy

Two main methods to determine  $\Delta G_{\text{RXN}}^{\circ}$

1. 
$$\Delta G_{\text{RXN}}^{\circ} = \Delta H_{\text{RXN}}^{\circ} - T\Delta S_{\text{RXN}}^{\circ}$$

2. 
$$\Delta G_{\text{RXN}}^{\circ} = \sum \Delta G_f^{\circ} (\text{products}) - \sum \Delta G_f^{\circ} (\text{reactants})$$

Similar to  $\Delta H_f^{\circ}$  are tabulated for a host of molecules.  
Just like  $\Delta H_f^{\circ}$  for an element in its standard stat,  
the  $\Delta G_f^{\circ}$  for an element in its standard state is zero.

