### **Chapter 19: Free Energy and Thermodynamics II**

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Spontaneous processes: Entropy of the <u>universe</u> increases ( $\Delta S_{univ} > 0$ )

Strange question: Why is the freezing of water spontaneous at 0  $^{\circ}C$ ?

- Entropy decreases, right?
- Yes, but the water is the <u>system</u>, what about the surroundings?

 $\angle \Delta S_{sys}$  decreases

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$



# Heat transfer and changes in the entropy of the surroundings

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

- Spontaneous process:  $\Delta S_{univ} > 0$
- $\Delta S_{sys}$  can be negative as long as  $\Delta S_{surr}$  is more positive than  $\Delta S_{sys}$  is negative:

$$\Delta S_{surr} > -\Delta S_{sys}$$



# Heat transfer and changes in the entropy of the surroundings



Back to freezing of water:

•  $\Delta S_{sys}$  is negative



 But the process is exothermic, releasing heat to the surroundings and therefore increasing the entropy of the surroundings

Exothermic process: Increases entropy of surroundings Endothermic process: Decreases entropy of surroundings



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### Temperature dependence of $\Delta S_{surr}$

Freezing of water is spontaneous at 0 °C, but non spontaneous at a higher temperature. Why?

- Heat released to the surroundings has less impact at higher temperatures
- For freezing of water:  $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$  Negative Positive and large at low T Positive and small at high T







 $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$  (for water freezing)

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## Quantifying ΔS<sub>surr</sub>



 $q_{sys}$  corresponds to heat of the system:

- $q_{sys} < 0$ : Exothermic ( $\Delta S_{surr} > 0$ )
- $q_{sys} > 0$ : Endothermic ( $\Delta S_{surr} < 0$ )

At constant pressure,  $q_{sys} = \Delta H_{sys}$ , so at constant *P*, *T*:

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$$



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### Calculate $\Delta S_{surr}$

**Example.** Given the reaction:  $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$   $\Delta H_{rxn} = -2044 \text{ kJ}$ 

calculate  $\Delta S_{surr}$  at 25 °C, determine signs of  $\Delta S_{sys}$  and  $\Delta S_{univ}$ .

**Solution.** Calculate the entropy change of the surroundings:

$$\Delta S_{surr} = -\Delta H_{surr} / T = -(-2,044 \times 10^3 \text{ J}) / (288 \text{ K}) = 7080 \text{ J} / \text{K}.$$

The number of moles increases in the reaction and therefore  $\Delta S_{sys} > 0$ . Since both  $\Delta S_{surr}$  and  $\Delta S_{sys}$  are positive then  $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$ . This means that the process is spontaneous.

## **Gibbs Free Energy**

For convenience, let's drop the sys and assume if you see  $\Delta S$  or  $\Delta H$  it is for the system.

Gibbs Free Energy: G = H - TS (system) Therefore, the change in *G* is (system):

At constant *T* and *P*:  $\Delta G = -T\Delta S_{univ}$ 

Note: Predicting spontaneity based on system observables!

Josiah Willard Gibbs 1839 – 1903 Connecticut, USA









## **Gibbs Free Energy**



The above result can be obtained by combining:  $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$  and  $\Delta S_{surr} = -\Delta H_{sys} / T$ 

So, use  $\Delta G$  (constant *T*, *P*) as a criterion for spontaneity!

 $\Delta G$  is proportional to  $-\Delta S_{univ}$  and hence:

- If  $\Delta G < 0$ , process is spontaneous
- If  $\Delta G > 0$ , process is nonspontaneous





# Effect of $\Delta H$ , $\Delta S$ , and T on spontaneity

#### <u>Case 1: ΔH negative, ΔS positive</u>



- Exothermic process and the entropy increases
- Process is spontaneous at all temperatures



# Effect of $\Delta H$ , $\Delta S$ , and T on spontaneity



- Endothermic process and entropy of system increases
- Process is non-spontaneous at all temperatures





# Effect of $\Delta H$ , $\Delta S$ , and T on spontaneity



- Exothermic process and entropy of system decreases
- Process is spontaneous at low temperatures
- Process is non-spontaneous at high temperatures





# Effect of $\Delta H$ , $\Delta S$ , and T on spontaneity



- Endothermic process and entropy of system increases
- Process is spontaneous at high temperatures
- Process is non-spontaneous at low temperatures





# Summary on Gibbs free energy ( $\Delta G$ )

#### $\Delta G = \Delta H - T \Delta S$

<b>TABLE 18.1</b> The Effect of $\Delta H$ , $\Delta S$ , and $T$ on Spontaneity				
ΔН	ΔS	Low Temperature	High Temperature	Example
_	+	Spontaneous ( $\Delta G < 0$ )	Spontaneous ( $\Delta G < 0$ )	$2 \text{ N}_2 \text{O}(g) \longrightarrow 2 \text{ N}_2(g) + \text{O}_2(g)$
+	-	Nonspontaneous ( $\Delta G > 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$3 O_2(g) \longrightarrow 2 O_3(g)$
_	_	Spontaneous ( $\Delta G < 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$H_2O(I) \longrightarrow H_2O(s)$
+	+	Nonspontaneous ( $\Delta G > 0$ )	Spontaneous ( $\Delta G < 0$ )	$H_2O(I) \longrightarrow H_2O(g)$

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Consider the reaction:  $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ . Given  $\Delta H = -137.5$  kJ and  $\Delta S = -120.5$  J/K, calculate  $\Delta G$  at 25 °C. Is the reaction spontaneous? How does  $\Delta G$  vary with temperature?

Example

**Solution:** 
$$T = 298$$
 K, so:  
 $\Delta G = \Delta H - T\Delta S = -137.5 \times 10^3 J - (298 K)(-120.5 J/K)$   
 $\Delta G = -101,591 J$ 

Since  $\Delta G < 0$  this reaction is spontaneous at given the temperature. Increasing *T* increases  $\Delta G$ , so the reaction will become non-spontaneous at high temperatures.



## **Calculating entropy in a reaction**

Third Law: As temperature approaches absolute zero, entropy approaches a constant. The entropy of a perfectly ordered crystal at absolute zero is zero.

Nothing in the universe has zero entropy.

Entropy is inherent to the molecules in a reaction:

- Available in thermodynamic tables
- Has units of J / (mol K) (molar entropy)
- "Extensive" property depends on how much is present but molar entropy is not.





### Standard state -

- We will be calculating  $\Delta S^{\circ}$  values (also for  $\Delta H^{\circ}$  and  $\Delta G^{\circ}$ )
- Standard State (or Standard Conditions)
  - Gas: Pressure = 1 atm
  - Liquid or Solid: Pure substance in its most stable state at P = 1 atm.
  - Solution: 1 M concentration
  - Does not specify temperature but usually T = 25 °C.

Then, in a reaction (depending on the number of moles)

$$\Delta S_{rxn}^{\circ} = S_{products}^{\circ} - S_{reactants}^{\circ}$$





**TABLE 18.2** Standard Molar Entropy Values (S°) for Selected Substances at 298 K

Substance	S°(J/mol · K)	Substance	S°(J/mol · K)	Substance	S°(J/mol · K)
Gases		Liquids		Solids	
$H_2(g)$	130.7	H <sub>2</sub> O( <i>I</i> )	70.0	MgO(s)	27.0
Ar(g)	154.8	CH <sub>3</sub> OH( <i>I</i> )	126.8	Fe(s)	27.3
$CH_4(g)$	186.3	Br <sub>2</sub> ( <i>I</i> )	152.2	Li(s)	29.1
$H_2O(g)$	188.8	C <sub>6</sub> H <sub>6</sub> ( <i>I</i> )	173.4	Cu(s)	33.2
N <sub>2</sub> (g)	191.6			Na(s)	51.3
NH <sub>3</sub> (g)	192.8			K(s)	64.7
$F_2(g)$	202.8			NaCl(s)	72.1
0 <sub>2</sub> (g)	205.2			CaCO <sub>3</sub> (s)	91.7
$Cl_2(g)$	223.1			FeCl <sub>3</sub> (s)	142.3
$C_2H_4(g)$	219.3				

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Note: The units are J / (mol K). These are molar entropies.



## **Standard Entropy of a Reaction**

$$\Delta S_{rxn}^{\circ} = \sum n_p S^{\circ}(products) - \sum n_r S^{\circ}(reactants)$$

### Reaction must be specified and balanced!

- $n_p$  is the number of moles of each product
- $n_r$  is the number of moles of each reactant
- Note: Standard states
- Similar to calculation for enthalpy of reaction
- Unlike enthalpy of reaction, all elements have an entropy at 25 °C!



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### Example

Calculate the standard entropy of reaction for:

 $2 \ \mathrm{NH}_3(g) \longrightarrow \mathrm{N}_2\mathrm{H}_4(g) + \mathrm{H}_2(g)$ 

Compound	Sº (J/mol K)
NH₃( <i>g</i> )	192.8
$N_2H_4(g)$	238.5
H <sub>2</sub> (g)	130.7

$$\Delta S_{rxn}^{\circ} = \sum n_p S^{\circ}(products) - \sum n_r S^{\circ}(reactants)$$

 $\Delta S_{rxn}^{\circ} = (238.5 + 130.7 - 2 \times 192.8) \text{ J / (mol K)}$ = -16.4 J / (mol K)



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### **Relative entropies**

As we discussed before:  $S_{gas} > S_{liquid} > S_{solid}$ 

- As seen in the table: H<sub>2</sub>O (g) > H<sub>2</sub>O (/) (at 298 K)
- Trend with molar mass: Higher molar mass is generally higher S

		S° (J∕mol·K)	
_	He(g)	126.2	
	Ne(g)	146.1	
	Ar(g)	154.8	
	Kr(g)	163.8	
-	Xe(g)	169.4	

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## Allotropes

 Some elements exist in two (or more) forms within the same state called *allotropes*. Usually different crystal forms of a solid.

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• Allotropes will have different S° values based on structure

Examples:

- C(s)
- S<sub>6</sub>(s) vs. S<sub>8</sub>(s)
- O<sub>3</sub>(g) vs. O<sub>2</sub>(g)









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## **Molecular complexity**

In general, the more complex the molecule, the higher the entropy:

	Molar Mass (g/mol)	S°(J/mol · K)
Ar(g)	39.948	154.8
NO(g)	30.006	210.8

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	Molar Mass (g/mol)	S°(J/mol · K)
CO(g)	28.01	197.7
$C_2H_4(g)$	28.05	219.3

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### Dissolution

Dissolved ions in solution have a higher entropy than the crystalline solid:

lons can move more freely in liquid

	S°(J/mol · K)
KClO <sub>3</sub> (s)	143.1
KClO <sub>3</sub> (aq)	265.7

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# **Recall: Standard enthalpy of reaction**



$$\Delta H_{rxn}^{\circ} = \sum n_p \Delta H_f^{\circ}(products) - \sum n_r \Delta H_f^{\circ}(reactants)$$

- $\Delta H_f^{\circ}$  = Heat of formation of a substance in standard state
- $n_p$  is the number of moles of each product
- $n_r$  is the number of moles of each reactant
- For an element in its standard state,  $\Delta H_f^o = 0$

#### <u>Remember: $\Delta H_{rxn}^{\circ} < 0$ : exothermic $\Delta H_{rxn}^{\circ} > 0$ : endothermic</u>



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### Example

Calculate the standard enthalpy of reaction for:  $2 \text{ NH}_3(g) \longrightarrow N_2H_4(g) + H_2(g)$ 

$$\Delta H_{rxn}^{\circ} = \sum n_p \Delta H_f^{\circ}(products) - \sum n_r \Delta H_f^{\circ}(reactants)$$

Compound	Δ <i>H</i> <sup>°</sup> (kJ / mol)
NH₃( <i>g</i> )	-45.9
N <sub>2</sub> H <sub>4</sub> (g)	50.6
H <sub>2</sub> (g)	0

 $\Delta H^{\circ}_{rxn} = (50.6 + 0 - 2 \times (-45.9)) \text{ kJ / mol} = 142.4 \text{ kJ / mol}$ 



## Calculating $\Delta G_{rxn}^{\circ}$



Now we have calculated  $\Delta S_{rxn}^{\circ}$  and  $\Delta H_{rxn}^{\circ}$ :

Put them together (with *T*) to get the Gibbs Free Energy change in a chemical reaction:

$$\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}$$

Note that there are two ways to get  $\Delta G_{rxn}^{\circ}$ .



### Calculating $\Delta G_{rxn}^{\circ}$

$$\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}$$

2  $\operatorname{NH}_3(g) \longrightarrow \operatorname{N}_2\operatorname{H}_4(g) + \operatorname{H}_2(g)$   $\Delta S^{\circ}_{rxn} = -16.4 \ J/mol \cdot K$  $\Delta H^{\circ}_{rxn} = 142.4 \ kJ/mol$ 

Is the reaction spontaneous at 25 °C (298 K)?

$$\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}$$
  
= 142.4 kJ/mol - 298 K × (-0.0164 kJ / (mol K))  
= 147.3 kJ/mol  
(be coreful: edd. l/mol to l/mol or k l/mol to k l/mol)

(be careful: add J/mol to J/mol or kJ/mol to kJ/mol) Here  $\Delta G^{\circ}_{rxn} > 0$ , so this is not spontaneous.

### Calculate the $\Delta G_{rxn}^{\circ}$ given Free Energies of Formation

Sometimes you will be given Free Energies of Formation.

The reaction free energy can be calculated from:



$$\Delta G_{rxn}^{\circ} = \sum (n_p \Delta G_f^{\circ}(products)) - \sum (n_r \Delta G_f^{\circ}(reactants))$$

### A similar formula to those for calculating $\Delta H^{o}_{rxn}$ and $\Delta S^{o}_{rxn}$ .