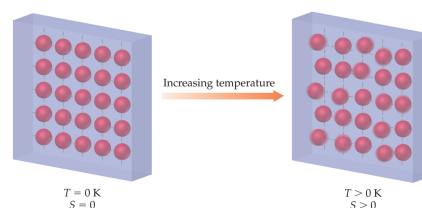


## 17.2 - Free Energy

### Third Law of Thermodynamics

MISPLACED! Should have been after second Law.

The entropy of a pure crystalline substance at absolute zero is 0.



### Free Energy ( $G$ )

So far we have used entropy to predict if a reaction is spontaneous. However, even if a reaction is favored according to entropy, at the wrong temperature it will not occur (Ex: a mixture of hydrogen and oxygen at room temperature will not burst into flames unless ignited).

Another thermodynamic quantity that takes into account the temperature dependence of entropy, as well as inherent enthalpic properties of a system, is Free Energy (symbol =  $G$ , for Josiah Willard Gibbs, an American Scientist).

### Free Energy ( $G$ )

At constant temperature,

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

$H$  - Enthalpy (J)  
 $T$  - Temperature (K)  
 $S$  - Entropy (J/K)

All quantities refer to the system.

### Relationship between Free Energy ( $G$ ) and Spontaneity

Starting with Free Energy relation, and drawing from earlier relations:

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

Divide by  $T$ : 
$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

Earlier we saw: 
$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

Then substituting: 
$$-\frac{\Delta G}{T} = \Delta S_{\text{surr}} + \Delta S$$

### Relationship between Free Energy ( $G$ ) and Spontaneity

We also saw: 
$$\Delta S_{\text{surr}} + \Delta S = \Delta S_{\text{univ}}$$

Subbing in: 
$$-\frac{\Delta G}{T} = \Delta S_{\text{univ}}$$

So: 
$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T} \text{ at constant } T \text{ and } P$$

Thus: processes occurring at constant  $T$  and  $P$  are spontaneous in the direction in which free energy decreases.

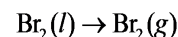
In other words, negative  $\Delta G$  means positive  $\Delta S_{\text{univ}}$ , so a process with  $-\Delta G$  will be spontaneous.

**Possible Combinations of  $\Delta H$  and  $\Delta S$** 

Case	Result
$\Delta S$ positive, $\Delta H$ negative	Spontaneous at all temperatures
$\Delta S$ positive, $\Delta H$ positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
$\Delta S$ negative, $\Delta H$ negative	Spontaneous at low temperatures (where exothermicity is dominant)
$\Delta S$ negative, $\Delta H$ positive	Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures)

**1. Free Energy & Spontaneity**

At what temperatures is the following process spontaneous at 1 atm?



$$\Delta H^\circ = 31.0 \text{ kJ/mol and } \Delta S^\circ = 93.0 \text{ J/K} \cdot \text{mol}$$

In other words, what is the boiling point of liquid  $\text{Br}_2$  at standard conditions?

**1. Free Energy & Spontaneity**

Vaporization will be spontaneous at all temperatures where  $\Delta G$  is negative, and nonspontaneous where  $\Delta G$  is positive. Thus, the vaporization threshold is where  $\Delta G$  is zero:

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

$$0 = \Delta H - T\Delta S$$

$$T\Delta S = \Delta H$$

$$T = \frac{\Delta H}{\Delta S} = \frac{31.0 \text{ kJ/mol}}{93.0 \text{ J/K} \cdot \text{mol}} \cdot \frac{1000 \text{ J}}{1 \text{ kJ}} = \boxed{333 \text{ K}}$$

**2. Rotten Eggs!**

Ethanethiol ( $\text{C}_2\text{H}_5\text{SH}$ ; also called ethyl mercaptan) is commonly added to natural gas to provide the "rotten egg" smell of a gas leak.

The boiling point of ethanethiol is  $35^\circ\text{C}$  and its heat of vaporization is  $27.5 \text{ kJ/mol}$ .

What is the entropy of vaporization for this substance?

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

$$0 = \Delta H - T\Delta S$$

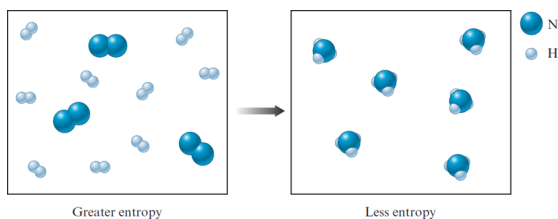
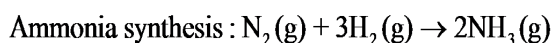
$$T\Delta S = \Delta H$$

$$\Delta S = \frac{\Delta H}{T} = \frac{27.5 \text{ kJ/mol}}{308 \text{ K}} \cdot \frac{1000 \text{ J}}{1 \text{ kJ}} = \boxed{89.3 \text{ J/K} \cdot \text{mol}}$$

**Entropy Changes & Chemical Reactions**

Positional probability determines the changes that occur in a chemical system.

Fewer the molecules, fewer the possible configurations.

**Entropy Changes in Reactions Involving Gaseous Molecules**

Change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products.

If the number of product molecules is greater than the number of reactant molecules:

Positional entropy increases,  
 $\Delta S$  is positive.

**3. Predicting the Sign of  $\Delta S^\circ$** 

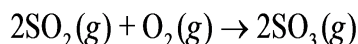
Predict the sign of  $\Delta S^\circ$  for each of the following reactions:

Thermal decomposition of solid calcium carbonate:



Positive: Product has one mole of gas.

Oxidation of  $\text{SO}_2$  in air:



Negative: three moles of gas reduce to two moles.

**Methods for Calculating  $\Delta G^\circ$** 

A. Use the following formula:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

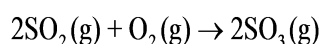
B. Treat free energy as a state function and use Hess's law.

C. Use standard free energy of formation equation and information in Appendix 4.

$$\Delta G = \sum n \Delta G^\circ_{\text{products}} - \sum m \Delta G^\circ_{\text{reactants}}$$

**4. Calculating  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$** 

Consider the following reaction carried out at  $25^\circ\text{C}$  and 1 atm:



Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  using the following data:

Substance	$H_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)
$\text{SO}_2(g)$	-297	248
$\text{SO}_3(g)$	-396	257
$\text{O}_2(g)$	0	205

**4. Calculating  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  Solution**

The value of  $\Delta H^\circ$  can be calculated from the enthalpies of formation using the following formula:

$$\Delta H^\circ = \sum n_p \Delta H^\circ_{f(\text{products})} - \sum n_r \Delta H^\circ_{f(\text{reactants})}$$

$$\Delta H^\circ = 2\Delta H^\circ_{f(\text{SO}_3(g))} - 2\Delta H^\circ_{f(\text{SO}_2(g))} - \Delta H^\circ_{f(\text{O}_2(g))}$$

$$= 2 \text{ mol}(-396 \text{ kJ/mol}) - 2 \text{ mol}(-297 \text{ kJ/mol}) - 0$$

$$= -792 \text{ kJ} + 594 \text{ kJ} = \boxed{-198 \text{ kJ}}$$

**4. Calculating  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  Solution**

The value of  $\Delta S^\circ$  can be calculated similarly:

$$\Delta S^\circ = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = 2S^\circ_{\text{SO}_3(g)} - 2S^\circ_{\text{SO}_2(g)} - 2S^\circ_{\text{O}_2(g)}$$

$$= 2 \text{ mol} (257 \text{ J/K} \cdot \text{mol}) - 2 \text{ mol} (248 \text{ J/K} \cdot \text{mol})$$

$$- 1 \text{ mol} (205 \text{ J/K} \cdot \text{mol})$$

$$= 514 \text{ J/K} - 496 \text{ J/K} - 205 \text{ J/K} = \boxed{-187 \text{ J/K}}$$

**4. Calculating  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  Solution**

The value of  $\Delta G^\circ$  can now be calculated:

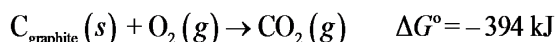
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -198 \text{ kJ} - (298 \text{ K}) \left( -187 \frac{\text{J}}{\text{K}} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right)$$

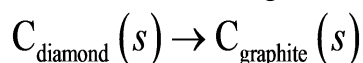
$$= -198 \text{ kJ} + 55.7 \text{ kJ} = \boxed{-142 \text{ kJ}}$$

### 5. Calculating $\Delta G^\circ$

Use the following data (at 25°C):

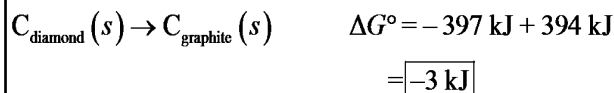
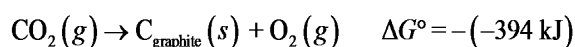
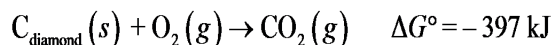


Calculate  $\Delta G^\circ$  for the following reaction:



### 5. Calculating $\Delta G^\circ$ Solution

Reverse equation 2 to make graphite a product, as required, and then add the new equation to equation.



### 5. Calculating $\Delta G^\circ$ Solution

Since  $\Delta G^\circ$  is negative for this process, diamond should spontaneously change to graphite at 25°C and 1 atm.

However, the reaction is so slow under these conditions that we do not observe the process.

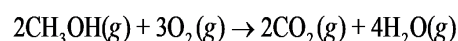
This is another example of kinetic rather than thermodynamic control of a reaction.

We can say that diamond is kinetically stable with respect to graphite even though it is thermodynamically unstable.

### 6. Calculating $\Delta G^\circ$ of Formation

Methanol is a high-octane fuel used in high-performance racing engines.

Calculate  $\Delta G^\circ$  for the following reaction:



The following energies of formation are provided:

Substance	$\Delta G_f^\circ$ (kJ/mol)
$\text{CH}_3\text{OH}(g)$	-163
$\text{O}_2(g)$	0
$\text{CO}_2(g)$	-394
$\text{H}_2\text{O}(g)$	-229

### 6. Calculating $\Delta G^\circ$ of Formation Solution

$$\begin{aligned} \Delta G &= \sum n \Delta G^\circ_{\text{products}} - \sum m \Delta G^\circ_{\text{reactants}} \\ \Delta G &= 2 \text{ mol} (-394 \text{ kJ/mol}) + 4 \text{ mol} (-229 \text{ kJ/mol}) \\ &\quad - 2 \text{ mol} (-163 \text{ kJ/mol}) - 0 = -1378 \text{ kJ} \end{aligned}$$

The large magnitude and the negative sign of  $\Delta G^\circ$  indicate that this reaction is very favorable thermodynamically.

### Homework

Read ONLY 17.7 in your textbook

17.2 Problems in your Booklet  
Due: Next Class.