

**CALCULATING STANDARD FREE ENERGY CHANGES**

- The standard free energy change ( $\Delta G^\circ$ ) for a reaction is the criterion for its spontaneity, and can be calculated by 3 different methods.

**Method 1:**

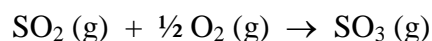
- Earlier in this chapter we learned how to use tabulated values of  $\Delta H^\circ_f$  and  $S^\circ$  to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for a reaction.
- We can now use the  $\Delta H^\circ$  and  $\Delta S^\circ$  values to calculate the  $\Delta G^\circ$  value for a reaction, using the equation:

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

- Since  $\Delta H^\circ_f$  and  $S^\circ$  values are tabulated at 25°C, the equation above should only be valid at 25°C. However, since  $\Delta H^\circ_f$  and  $S^\circ$  values are affected very little by temperature, we can estimate the  $\Delta G^\circ$  values for temperatures other than 25°C.

**Examples:**

- Given  $\Delta H^\circ_f$  and  $S^\circ$  values shown below, calculate  $\Delta G^\circ$  for the reaction shown below, and determine if the reaction is spontaneous.



Reactant or product	$\Delta H^\circ_f$ (kJ/mol)	$S^\circ$ (J/mol · K)
$\text{SO}_2(\text{g})$	-296.8	248.2
$\text{O}_2(\text{g})$	0	205.2
$\text{SO}_3(\text{g})$	-395.7	256.8

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- Use the data in Appendix IIA of your text to calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  at 25°C for the reaction shown below. Is the reaction spontaneous? If not, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25°C?



**CALCULATING STANDARD FREE ENERGY CHANGES**
**Method 2:**

- Because free energy is a state function, change in free energy of reactions ( $\Delta G^\circ$ ) can also be calculated from the free energy of the reactants and products. In order to do this, we define the *free energy of formation* ( $\Delta G_f^\circ$ ) for a substance as follows:

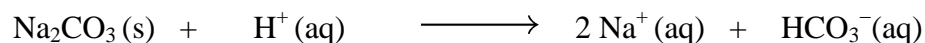
**The free energy of formation ( $\Delta G_f^\circ$ ) is the change in free energy when 1 mole of a compound in its standard state forms from its constituent elements in their standard states. The free energy of formation of pure elements in their standard states is zero.**

- The free energy change of a reaction can then be calculated using the equation below:

$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$

**Examples:**

- Calculate the standard free energy change ( $\Delta G^\circ$ ) for the following reaction at 25 °C, using standard free energies of formation given below:



$$\Delta G_f^\circ (\text{kJ/mol}) : \quad -1048.1 \quad 0 \quad -261.9 \quad -587.1$$

$$\Delta G^\circ = [(2) \times (-261.9) + (-587.1)] - [(-1048.1) + 0] \text{ kJ} = -62.8 \text{ kJ}$$

- Calculate the standard free-energy change ( $\Delta G^\circ$ ) for the reaction shown below, and determine whether it is spontaneous or not. (Use  $\Delta G_f^\circ$  values in your textbook).



- Calculate the standard free-energy change ( $\Delta G^\circ$ ) for the reaction shown below, and compare with the value obtained by method 1 on the previous page. (Use  $\Delta G_f^\circ$  values in your textbook).

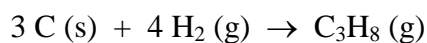


**CALCULATING STANDARD FREE ENERGY CHANGES**
**Method 3:**

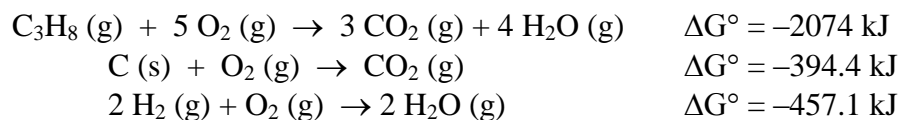
- Since free energy is a state function, the following relationships can be used to calculate  $\Delta G$  for a reaction:
  - If a chemical equation is multiplied by some factor, then  $\Delta G$  for the reaction is also multiplied by the same factor.
  - If a chemical equation is reversed, then  $\Delta G$  changes sign.
  - If a chemical equation can be expressed as the sum of a series of steps, then  $\Delta G$  for the overall equation is the sum of the free energies of reactions for each step.

**Examples:**

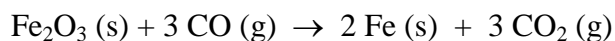
1. Find  $\Delta G^\circ$  for the reaction shown below:



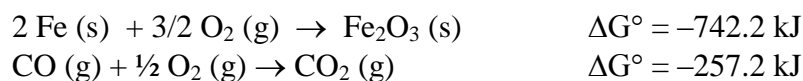
Use the following reactions with known  $\Delta G^\circ$  values:



2. Determine  $\Delta G^\circ$  for the reaction shown below:



Use the following reactions with known  $\Delta G^\circ$  values:



## FREE ENERGY and USEFUL WORK

- In a spontaneous reaction:
  - the “free” energy is lowered as reactants change to products,
  - the change in “free” energy is released as free-energy change ( $\Delta G$ )
  - this “ $\Delta G$ ” can be harnessed to perform useful work

**A spontaneous reaction can be used to obtain useful work**

- The change in free energy of a chemical reaction represents the maximum amount of energy available (or free) to do work (if  $\Delta G^\circ$  is negative).

Maximum useful work =

$$w_{\max} = \Delta G^\circ$$

- In an **ideal** situation:

$\Delta G^\circ$  → Useful work

completely  
converted into

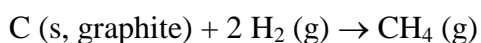
- In **real** situations:

$\Delta G^\circ$  → Some Useful Work + Some Entropy

converted  
into

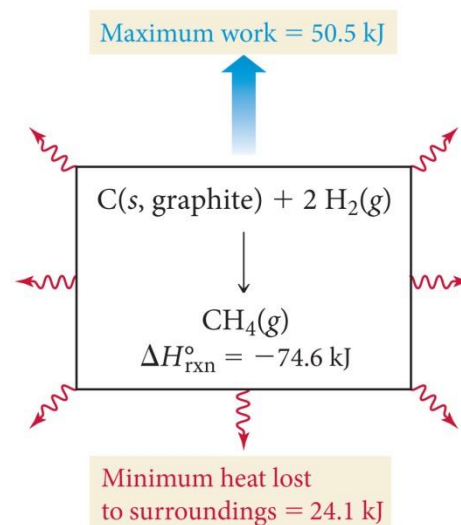
### Conclusions:

1. In theory, all of the free-energy decrease liberated during a spontaneous chemical change can be used to do work (this would be  $w_{\max}$ )
2. In practice, less work is obtained and the difference appears as an increase in entropy.



$$\Delta H^\circ = -74.6 \text{ kJ} \quad \Delta S^\circ = -80.8 \text{ J/K} \quad \Delta G^\circ = -50.5 \text{ kJ}$$

- Why is only 50.5 kJ available as free energy, even though 74.6 kJ is produced in the reaction?
- How is this reaction spontaneous ( $\Delta G^\circ < 0$ ) when entropy decreases?



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## FREE ENERGY CHANGES FOR NONSTANDARD STATES

- The standard free energy changes for a reaction ( $\Delta G^\circ$ ) are only useful for a very narrow set of conditions where reactants and products are in their standard states.
- For example, consider the standard free energy change for evaporation of liquid water:



- Since  $\Delta G^\circ$  for this process is positive, it is nonspontaneous. Yet when water is spilled under ordinary conditions, it evaporates spontaneously. Why?
- This is because ordinary conditions are not standard states. For example, for water vapor, standard conditions are those where  $P_{\text{H}_2\text{O}}$  would be 1 atm. Based on the  $\Delta G^\circ$  value given above, under these conditions, the water vapor would condense spontaneously.
- Free energy changes under nonstandard conditions ( $\Delta G$ ) can be calculated from  $\Delta G^\circ$  according to the equation below:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$Q$  = Thermodynamic Reaction Quotient  
for reactions involving gases  $Q$  is obtained from partial pressures.  
for reactions in solutions,  $Q$  is obtained from molar concentrations

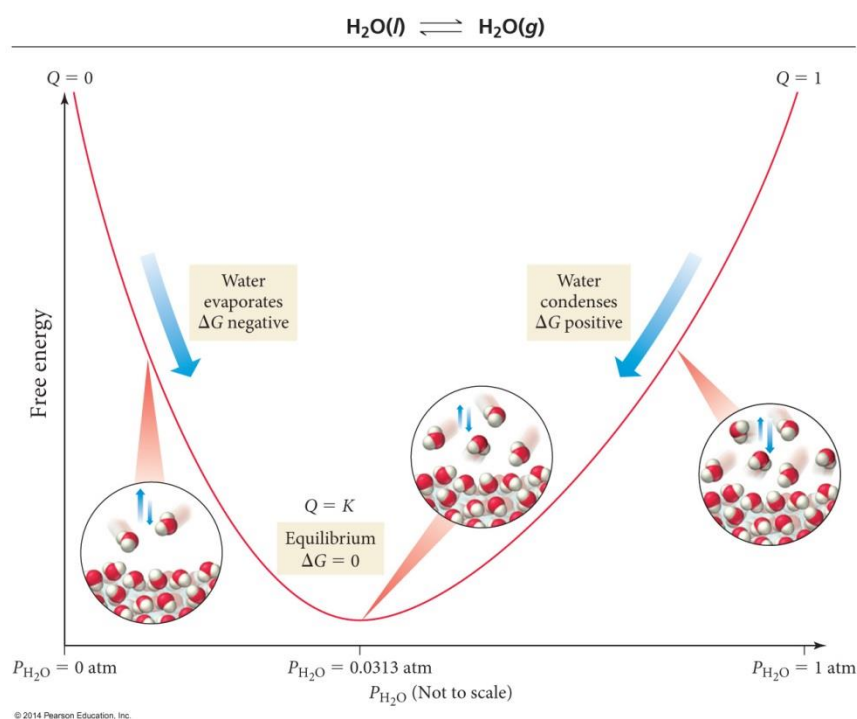
$R$  = Gas Law Constant in units of energy = 8.314 J/mol K

$\Delta G^\circ$  = Standard Free-Energy Change

$\Delta G$  = Free-Energy Change when Reactants in nonstandard states are changed to products in non-standard states

## FREE ENERGY CHANGES FOR NONSTANDARD STATES

- The relationship of free energy change for evaporation of water and pressure of water can be seen from diagram below:



- Under **standard condition**,  $Q = P_{\text{H}_2\text{O}} = 1 \text{ atm}$  and  $\Delta G = \Delta G^\circ$ , as expected.

$$\Delta G = \Delta G^\circ + RT \ln (1) = +8.59 \text{ kJ/mol}$$

- At **equilibrium**, where water vapor has a pressure of 0.0313 atm,  $\Delta G = 0$  as shown below:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln (0.0313) \\ &= +8.59 + (8.314 \text{ J/molK})(298) \ln (0.0313) \\ &= +8.59 \text{ kJ/mol} - 8.59 \text{ kJ/mol} = 0 \end{aligned}$$

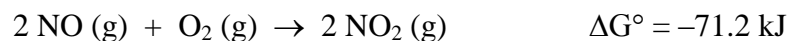
- Under **nonstandard condition**,  $P_{\text{H}_2\text{O}} = 0.005 \text{ atm}$  and  $\Delta G$  can be calculated as shown below:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln (0.005) \\ &= +8.59 + (8.314 \text{ J/molK})(298) \ln (0.005) \\ &= +8.59 \text{ kJ/mol} - 13.1 \text{ kJ/mol} = -4.5 \text{ kJ/mol} \end{aligned}$$

- Under these conditions, since  $\Delta G < 0$ , evaporation would be spontaneous.

**FREE ENERGY CHANGES FOR NONSTANDARD STATES****Examples:**

1. For the reaction shown below:



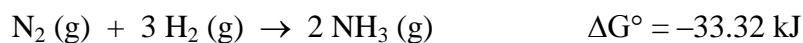
Calculate  $\Delta G$  under the following conditions:

$$P_{\text{NO}} = 0.100 \text{ atm}$$

$$P_{\text{O}_2} = 0.100 \text{ atm}$$

$$P_{\text{NO}_2} = 2.00 \text{ atm}$$

2. Calculate  $\Delta G$  for the reaction shown below if the reaction mixture consists of 1.0 atm  $\text{N}_2$ , 3.0 atm  $\text{H}_2$  and 1.0 atm  $\text{NH}_3$ .



## FREE ENERGY AND EQUILIBRIUM

- $\Delta G^\circ$  determines the spontaneity of a reaction when reactants and products are in their standard states.
- Previously we learned that equilibrium constant ( $K$ ) determines how far a reaction proceeds, also a measure of spontaneity.
- Therefore, it would follow that free energy changes and equilibrium constant are related. This relationship is shown below:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium  $0 = \Delta G^\circ + RT \ln K$

$$\Delta G^\circ = -RT \ln K$$

- It follows that:

1. For reactions involving only gases:

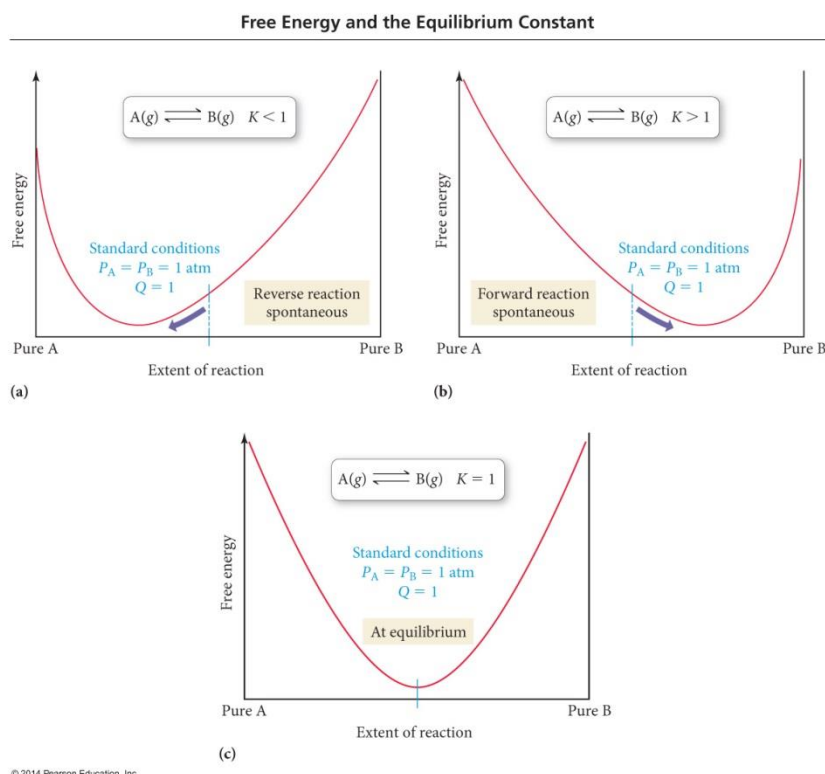
$$\mathbf{K = K_p}$$

2. For reactions involving only solutes in liquid solutions:

$$\mathbf{K = K_c}$$

3. For net ionic equations:

$$\mathbf{K = K_{sp}}$$





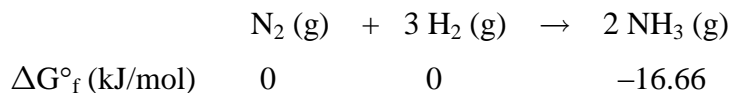
<b>RELATIONSHIP OF <math>\Delta G^\circ</math>, K, AND SPONTANEITY</b>
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<b><math>\Delta G^\circ = -RT \ln K</math></b>
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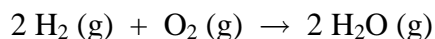
When $K > 1$	When $K \approx 1$	When $K < 1$
Reactants $\longrightarrow$ Products	Reactants $\rightleftharpoons$ Products	Reactants $\longleftarrow$ Products
$\log K > 0$	$\log K \approx 0$	$\log K < 0$
$\Delta G^\circ < 0$	$\Delta G^\circ \approx 0$	$\Delta G^\circ > 0$
Reaction is <b>spontaneous</b>	Reaction gives an <b>equilibrium mixture</b>	<b>Forward</b> reaction is <b>non-spontaneous</b> <b>Reverse</b> reaction is <b>spontaneous</b>

**Examples:**

- Use the standard free energies of formation given to determine the equilibrium constant (K) for the following reaction at 25 °C:



- Use the standard free energies in your text to calculate  $\Delta G^\circ$  and K for the following reaction at 25 °C:



**CHANGE OF FREE ENERGY WITH TEMPERATURE**

- How can  $\Delta G^\circ$  be found for temperatures other than standard temperatures (25 °C)?
- An approximate method used to calculate  $\Delta G^\circ_T$  is based on the assumption that both  $\Delta H^\circ$  and  $\Delta S^\circ$  are constant with respect to temperature (only approximately true)
- Then:  $\Delta G^\circ_T = \Delta H^\circ - T\Delta S^\circ$  (a convenient approximation for  $\Delta G^\circ_T$ )

**NOTE:**  $\Delta G^\circ_T$  is strongly temperature dependent

$\Delta G^\circ_T$  = Change in free Energy for a substance:

- at 1 atm of pressure (standard pressure) and
- at the specified temperature, T (nonstandard temperature)

SPONTANEITY  $\xrightarrow{\text{depends on the value of}}$   $\Delta G^\circ_T$   $\xrightarrow{\text{determined by}}$  TEMPERATURE

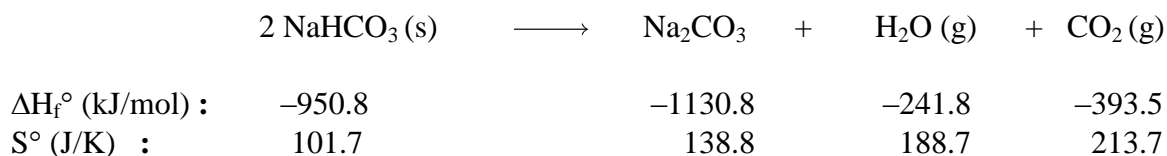
- It follows that **SPONTANEITY IS TEMPERATURE DEPENDENT!**

Meaning:

- Some chemical changes may be non-spontaneous at one temperature but spontaneous at another temperature.

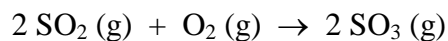
**Examples:**

1. Sodium Carbonate,  $\text{Na}_2\text{CO}_3$ , can be prepared by heating sodium hydrogen carbonate,  $\text{NaHCO}_3$ . Given the  $\Delta H_f^\circ$  and  $S^\circ$  values below, estimate the temperature at which  $\text{NaHCO}_3$  decomposes to products at 1 atm.



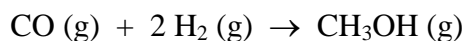
**CHANGE OF FREE ENERGY WITH TEMPERATURE****Examples:**

2. Given  $\Delta H^\circ$  and  $\Delta S^\circ$  values at  $25^\circ\text{C}$ , estimate  $\Delta G^\circ$  at 400 K for the reaction shown below:



$$\Delta H^\circ = -196.6 \text{ kJ} \qquad \Delta S^\circ = -189.6 \text{ J/K}$$

3. Methanol can be prepared from reaction of CO and  $\text{H}_2$ , as shown below:



$$\Delta H^\circ = -90.7 \text{ kJ} \qquad \Delta S^\circ = -221.5 \text{ J/K}$$

- a) Is this reaction spontaneous under standard conditions at  $25^\circ\text{C}$ ?
- b) Calculate  $\Delta G^\circ$  at 500 K. Is the reaction spontaneous under standard conditions at this temperature?

## Answers to In-Chapter Problems:

<i>Page</i>	<i>Example No.</i>	<i>Answer</i>
5	1	positive
	2	negative
	3	positive
7	1	$\Delta E = +71 \text{ J}$
	2	$\Delta E = -727 \text{ kJ}$
9	2	+37.60 kJ
	3a	+3.92 kJ
	3b	0 J
10	4	-122 J
	5	$\Delta E = -998 \text{ J}$
	6	d
12	2a	$\Delta H^\circ = -172.9 \text{ kJ}$
	2b	$\Delta H^\circ = +58.6 \text{ kJ}$
16	1a	positive
	1b	negative
	1c	positive
20	3a	$\Delta S_{\text{surr}} = +6.86 \times 10^3 \text{ J/K}$
	3b	$\Delta S_{\text{sys}} = +$
	3c	$\Delta S_{\text{univ}} = +$ ; reaction is spontaneous
24	1a	spontaneous at low temperature; nonspontaneous at high temperature
	1b	nonspontaneous at low temperature; spontaneous at high temperature
	1c	nonspontaneous at low temperature; spontaneous at high temperature
	2	$\Delta G = +53.3 \text{ kJ}$ ; reaction is not spontaneous The reaction becomes spontaneous at $T = 673 \text{ K}$

<i>Page</i>	<i>Example No.</i>	<i>Answer</i>
26	1a	
	1b	
27	1a	CO <sub>2</sub> (g) ; greater molar mass and complexity
	1b	CH <sub>3</sub> OH (g) ; gas phase
	1c	CO <sub>2</sub> (g); greater molar mass and complexity
	1d	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> ; greater complexity
28	2a	$\Delta S = \text{negative}$
	2b	$\Delta S = \text{inconclusive}$
	2c	$\Delta S = \text{positive}$
	3	$\Delta S^\circ = 178.8 \text{ J/K}$
29	1	$\Delta G^\circ = -70.9 \text{ kJ}$ ; spontaneous
	2	$\Delta H^\circ = 176.2 \text{ kJ}$ $\Delta S^\circ = 285.1 \text{ J/K}$ $\Delta G^\circ = 91.2 \text{ kJ}$ nonspontaneous; becomes spontaneous at high temperature
30	2	$\Delta G^\circ = +41.0 \text{ kJ}$ ; nonspontaneous
	3	$\Delta G^\circ = 91.2 \text{ kJ}$ ; value is comparable to that calculated by method 1
31	1	$\Delta G^\circ = -23 \text{ kJ}$
	2	$\Delta G^\circ = -29.4 \text{ kJ}$
35	1	$\Delta G = -50.7 \text{ kJ}$
	2	$\Delta G = -41.5 \text{ kJ}$
37	1	$K = 6.9 \times 10^5$
	2	$K = 1.39 \times 10^{80}$
38	1	$T = 401.1 \text{ K}$
39	2	$\Delta G^\circ_T = -120.8 \text{ kJ}$
	3a	$\Delta G^\circ = -24.7 \text{ kJ}$ ; reaction is spontaneous at 25°C
	3b	$\Delta G^\circ_T = +20.1 \text{ kJ}$ ; reaction is nonspontaneous at 500 K