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

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### Calculate the $\Delta G^{\circ}_{rxn}$ given steps in a reaction



- Similar to Hess's Law: If you have multiple reactions that add up to a reaction, you can calculate Gibbs Free Energies.
- If a chemical equation is multiplied by some factor, then  $\Delta G_{rxn}^{o}$  is multiplied by the same factor.
- If a chemical equation is reversed, change the sign of  $\Delta G_{rxn}^{o}$ .
- If a chemical reaction can be expressed as a sum of a series of steps, then  $\Delta G_{rxn}^{o}$  for the overall reaction is the sum of the free energies of reaction for each step.



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### Example

Find  $\Delta G_{rxn}^{\circ}$  for  $N_2O(g) + NO_2(g) \longrightarrow 3NO(g)$ given the reactions:

1. 
$$2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g) \quad \Delta G_{rxn}^\circ = -72.2 \ kJ$$

2. 
$$N_2(g) + O_2(g) \longrightarrow 2 NO(g) \quad \Delta G_{rxn}^\circ = +175.2 \ kJ$$

3.  $2 \operatorname{N}_2 O(g) \longrightarrow 2 \operatorname{N}_2(g) + O_2(g) \quad \Delta G_{rxn}^\circ = -207.4 \ kJ$ 

#### Solution.

1. Add reversed 1 to 3:

$$2NO_2 + 2N_2O \rightarrow 2NO + 2O_2 + 2N_2$$

 $\Delta G_{rxn^{o}} = (72.2 - 207.4) \text{ kJ} = -135.2 \text{ kJ}$ 

2. Divide this by 2: NO<sub>2</sub> + N<sub>2</sub>O  $\rightarrow$  NO + O<sub>2</sub> + N<sub>2</sub>  $\Delta G_{rxn}^{o}$  = -67.6 kJ

3. Add 2 to this: NO<sub>2</sub> + N<sub>2</sub>O  $\rightarrow$  3NO  $\Delta G_{rxn}^{\circ} = (175.2 - 67.6) \text{ kJ} = 107.6 \text{ kJ}$ 





## Free Energy Changes for Nonstandard states

Remember that  $\Delta G_{rxn}^{\circ}$  only applies to standard conditions. But what about nonstandard conditions?

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RTlnQ$$

- $R = 8.314 \text{ J} / (\text{mol K}) (= N_A k_B; "molar Boltzmann constant")$
- *T* = temperature (K)
- Q = reaction quotient (no unit)
- <u>Note</u>: Under standard conditions  $\Delta G_{rxn} = \Delta G_{rxn}^{o}$

and therefore Q = 1 (because ln(1) = 0).



#### **Example: Water evaporation into the atmosphere**

$$H_2O(\ell) \Longrightarrow H_2O(g) \quad \Delta G^{\circ}_{rxn} = +8.59 \ kJ$$

This is non-spontaneous, but you know that water evaporates at 25 °C! Why?

Non-standard condition!

Recall: 
$$Q = \frac{P_{H_2O}}{[H_2O(\ell)]} = P_{H_2O}$$

- Standard conditions:  $P_{H_{2O}} = 1$  atm
- In this example the partial pressure of water above the liquid is << 1 atm (also, it is constantly being removed; open system).







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### Water example continued



$$H_2O(\ell) \Longrightarrow H_2O(g) \quad \Delta G^{\circ}_{rxn} = +8.59 \ kJ$$

<u>**1. Standard conditions:</u>**  $Q = 1 (P_{H_{2O}} = 1 \text{ atm})$ </u>

$$\Delta G_{rxn} = 8.59 \ kJ + RTln(1) = 8.59 \ kJ$$

Spontaneous in reverse direction (would condense)

2. If very little water is in the atmosphere:  $P_{H_{2O}} = 0.005$  atm  $\Delta G_{rxn} = 8.59 \ kJ + RTln(0.005) = -4.54 \ kJ$ Spontaneous in forward direction (would evaporate)



#### Water example continued



$$H_2O(\ell) \Longrightarrow H_2O(g) \quad \Delta G^{\circ}_{rxn} = +8.59 \ kJ$$

#### <u>3. If $P_{H_2O}$ = 0.0313 atm:</u>

 $\Delta G_{rxn} = 8.59 \ kJ + RTln(0.0313) = 8.59 \ kJ - 8.59 \ kJ = 0 \ kJ$ 

Reaction is not spontaneous in either direction, so the reaction is at <u>equilibrium</u>.





# Relating $\Delta G_{rxn}^{\circ}$ to K (equilibrium)

• At equilibrium, Q = K and  $\Delta G_{rxn} = 0$  (non-spontaneous in either direction):

 $0 = \Delta G_{rxn}^{\circ} + RTlnK \qquad \Delta G_{rxn}^{\circ} = -RTlnK$ 

- Remember to use  $K_p$  for gases and  $K_c$  for solutions
- If K < 1, ΔG<sub>rxn</sub><sup>o</sup> is positive because ln(K) is negative
  Under standard conditions (Q = 1), Q > K, spontaneous in reverse direction
- If K > 1, ΔG<sub>rxn</sub><sup>o</sup> is negative because In(K) is positive
  Under standard conditions (Q = 1), Q < K, spontaneous in forward direction</li>
- If K = 1,  $\Delta G_{rxn}^{o}$  is zero, at equilibrium under standard conditions





#### Example

Determine the equilibrium constant at 25 °C (298 K) for:

$$N_2O_4(g) \Longrightarrow 2NO_2(g) \quad \Delta G^{\circ}_{rxn} = 2.8 \ kJ / mol$$

We use: 
$$\Delta G_{rxn}^{\circ} = -RTlnK$$

Solve for K:  $K = \exp(-\Delta G_{rxn}^{o}/(RT)) = \underline{0.32}$ 



### **Collection of useful formulas**



$$\Delta G_{rxn}^{\circ} = -RTlnK$$
$$\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$$
$$-RTlnK = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$$
$$lnK = -\frac{\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T}\right) + \frac{\Delta S_{rxn}^{\circ}}{R}$$

Two point form:  $ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_{rxn}^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$