

$\Delta G_f^\circ$  ~ similar to  $\Delta H_f^\circ$

can measure: element  $\rightarrow$  substance,  $\Delta G = \Delta G_f^\circ$   
std. state conds.

can calculate  $\Delta G_{rxn}^\circ$  via:

$$\Delta G_{rxn}^\circ = \left[ \sum n_p \cdot \Delta G_f^\circ(\text{Prods}) \right] - \left[ \sum n_r \cdot \Delta G_f^\circ(\text{Reacts}) \right]$$

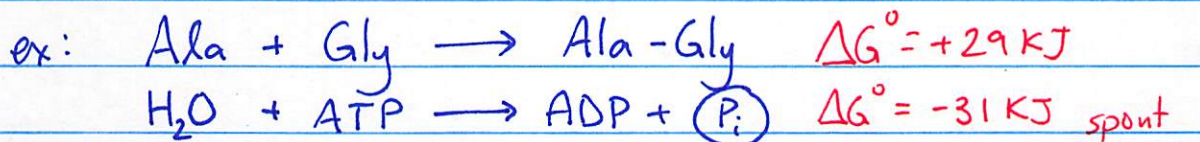
... only downside is these  $\Delta G_f^\circ$ 's are 25°C  
( $\Delta G_f^\circ = \Delta H^\circ - T\Delta S^\circ$ )

298K  
25°C

Pp 865-866 example calc.

Summing rxns (Hess's law)

coupled rxn

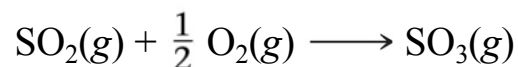


⊕



## Example 18.6 Calculating the Standard Change in Free Energy for a Reaction Using $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$

One of the possible initial steps in the formation of acid rain is the oxidation of the pollutant  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction:



Calculate  $\Delta G^\circ_{\text{rxn}}$  at 25 °C and determine whether the reaction is spontaneous.

### Solution

Begin by looking up (in Appendix IIB) the standard enthalpy of formation and the standard entropy for each reactant and product.

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

Calculate  $\Delta H^\circ_{\text{rxn}}$  using Equation 6.15.

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= \sum n_p \Delta H^\circ_f(\text{products}) - \sum n_r \Delta H^\circ_f(\text{reactants}) \\ &= [\Delta H^\circ_f, \text{SO}_3(\text{g})] - [\Delta H^\circ_f, \text{SO}_2(\text{g}) + \frac{1}{2}(\Delta H^\circ_f, \text{O}_2(\text{g}))] \\ &= -395.7 \text{ kJ} - (-296.8 \text{ kJ} + 0.0 \text{ kJ}) = -98.9 \text{ kJ}\end{aligned}$$

## Example 18.6 Calculating the Standard Change in Free Energy for a Reaction Using $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$

Continued

Calculate  $\Delta S^\circ_{\text{rxn}}$  using Equation 18.10.

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants}) \\ &= [S^\circ_{\text{SO}_3(\text{g})}] - [S^\circ_{\text{SO}_2(\text{g})} + \frac{1}{2}(S^\circ_{\text{O}_2(\text{g})})] \\ &= 256.8 \text{ J/K} - [248.2 \text{ J/K} + \frac{1}{2}(205.2 \text{ J/K})] = -94.0 \text{ J/K}\end{aligned}$$

Calculate  $\Delta G^\circ_{\text{rxn}}$  using the calculated values of  $\Delta H^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{rxn}}$  and Equation 18.11. Convert the temperature to kelvins.

$$\begin{aligned}T &= 25 + 273 = 298 \text{ K} \\ \Delta G^\circ_{\text{rxn}} &= \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} \\ &= -98.9 \times 10^3 \text{ J} - 298 \text{ K}(-94.0 \text{ J/K}) \\ &= -70.9 \times 10^3 \text{ J} = -70.9 \text{ kJ}\end{aligned}$$

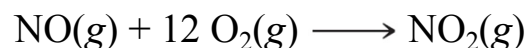
The reaction is spontaneous at this temperature because  $\Delta G^\circ_{\text{rxn}}$  is negative.

**Example 18.6** Calculating the Standard Change in Free Energy for a Reaction Using  $\Delta G^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}}$

Continued

**For Practice 18.6**

Consider the oxidation of NO to NO<sub>2</sub>:



Calculate  $\Delta G^{\circ}_{\text{rxn}}$  at 25 °C and determine whether the reaction is spontaneous at standard conditions.

## Example 18.7 Estimating the Standard Change in Free Energy for a Reaction at a Temperature Other Than 25 °C Using $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$

For the reaction in Example 18.6, estimate the value of  $\Delta G^\circ_{\text{rxn}}$  at 125 °C. Is the reaction more or less spontaneous at this elevated temperature; that is, is the value of  $\Delta G^\circ_{\text{rxn}}$  more negative (more spontaneous) or more positive (less spontaneous)?

### Solution

Estimate  $\Delta G^\circ_{\text{rxn}}$  at the new temperature using the calculated values of  $\Delta H^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{rxn}}$  from Example 18.6. For T, convert the given temperature to kelvins. Make sure to use the same units for  $\Delta H^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{rxn}}$  (usually joules).

$$\begin{aligned} T &= 125 + 273 = 398 \text{ K} \\ \Delta G^\circ_{\text{rxn}} &= \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} \\ &= -98.9 \times 10^3 \text{ J} - 398 \text{ K}(-94.0 \text{ J/K}) \\ &= -61.5 \times 10^3 \text{ J} \\ &= -61.5 \text{ kJ} \end{aligned}$$

Since the value of  $\Delta G^\circ_{\text{rxn}}$  at this elevated temperature is less negative (or more positive) than the value of  $\Delta G^\circ_{\text{rxn}}$  at 25 °C (which is  $-70.9 \text{ kJ}$ ), the reaction is less spontaneous.

### For Practice 18.7

For the reaction in For Practice 18.6, calculate the value of  $\Delta G^\circ_{\text{rxn}}$  at  $-55 \text{ °C}$ . Is the reaction more spontaneous (more negative  $\Delta G^\circ_{\text{rxn}}$ ) or less spontaneous (more positive  $\Delta G^\circ_{\text{rxn}}$ ) at the lower temperature?

## Example 18.8 Calculating $\Delta G^\circ_{\text{rxn}}$ from Standard Free Energies of Formation

Ozone in the lower atmosphere is a pollutant that can form by the following reaction involving the oxidation of unburned hydrocarbons:



Use the standard free energies of formation to determine  $\Delta G^\circ_{\text{rxn}}$  for this reaction at 25 °C.

### Solution

Begin by looking up (in Appendix IIB) the standard free energies of formation for each reactant and product. Remember that the standard free energy of formation of a pure element in its standard state is zero.

Reactant or product	$\Delta G_f^\circ$ (in kJ/mol)
$\text{CH}_4(g)$	-50.5
$\text{O}_2(g)$	0.0
$\text{CO}_2(g)$	-394.4
$\text{H}_2\text{O}(g)$	-228.6
$\text{O}_3(g)$	163.2

## Example 18.8 Calculating $\Delta G^\circ_{\text{rxn}}$ from Standard Free Energies of Formation

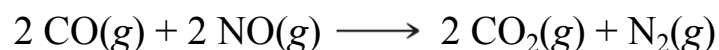
Continued

Calculate  $\Delta G^\circ_{\text{rxn}}$  by substituting into Equation 18.12.

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \sum n_p \Delta G^\circ_f(\text{products}) - \sum n_r \Delta G^\circ_f(\text{reactants}) \\ &= [\Delta G^\circ_{f, \text{CO}_2(g)} + 2(\Delta G^\circ_{f, \text{H}_2\text{O}(g)}) + 4(\Delta G^\circ_{f, \text{O}_3(g)})] - [\Delta G^\circ_{f, \text{CH}_4(g)} + 8(\Delta G^\circ_{f, \text{O}_2(g)})] \\ &= [-394.4 \text{ kJ} + 2(-228.6 \text{ kJ}) + 4(163.2 \text{ kJ})] - [-50.5 \text{ kJ} + 8(0.0 \text{ kJ})] \\ &= -198.8 \text{ kJ} + 50.5 \text{ kJ} \\ &= -148.3 \text{ kJ}\end{aligned}$$

### For Practice 18.8

One of the reactions that occurs within a catalytic converter in the exhaust pipe of a car is the simultaneous oxidation of carbon monoxide and reduction of NO (both of which are harmful pollutants):



Use standard free energies of formation to determine  $\Delta G^\circ_{\text{rxn}}$  for this reaction at 25 °C. Is the reaction spontaneous at Standard conditions?

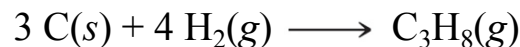
### For More Practice 18.8

In For Practice 18.8, you calculated  $\Delta G^\circ_{\text{rxn}}$  for the simultaneous oxidation of carbon monoxide and reduction of NO using standard free energies of formation. Calculate  $\Delta G^\circ_{\text{rxn}}$  for that reaction again at 25 °C, only this time use  $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$ . How do the two values compare? Use your results to calculate  $\Delta G^\circ_{\text{rxn}}$  at 500.0 K and explain why you could not calculate  $\Delta G^\circ_{\text{rxn}}$  at 500.0 K using tabulated standard free energies of formation.

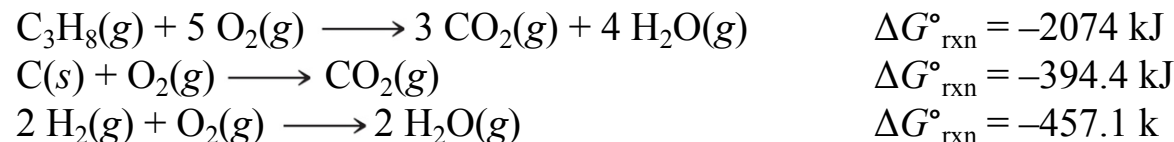


## Example 18.9 Calculating $\Delta G^\circ_{\text{rxn}}$ for a Stepwise Reaction

Find  $\Delta G^\circ_{\text{rxn}}$  for the reaction:



Use the following reactions with known  $\Delta G^\circ_{\text{rxn}}$  values:



### Solution

To work this problem, you need to manipulate the given reactions with known values of  $\Delta G^\circ_{\text{rxn}}$  in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

Since the first reaction has  $\text{C}_3\text{H}_8$  as a reactant, and the reaction of interest has  $\text{C}_3\text{H}_8$  as a product, reverse the first reaction and change the sign of  $\Delta G^\circ_{\text{rxn}}$ .



The second reaction has C as a reactant and  $\text{CO}_2$  as a product, as required in the reaction of interest. However, the coefficient for C is 1, and in the reaction of interest, the coefficient for C is 3. Therefore, multiply this equation and its  $\Delta G^\circ_{\text{rxn}}$  by 3.

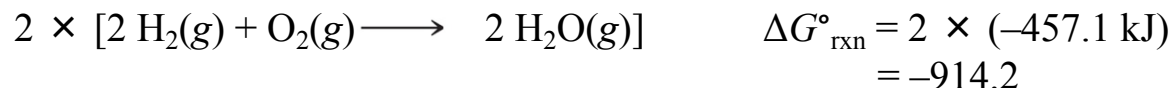




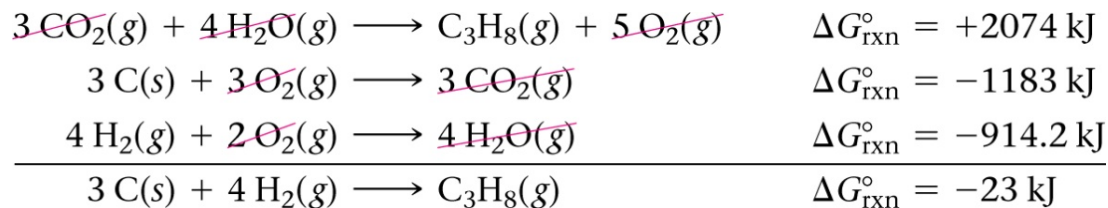
## Example 18.9 Calculating $\Delta G^\circ_{\text{rxn}}$ for a Stepwise Reaction

Continued

In the third reaction  $\text{H}_2(\text{g})$  is a reactant, as required. However, the coefficient for  $\text{H}_2$  is 2, and in the reaction of interest, the coefficient for  $\text{H}_2$  is 4. Multiply this reaction and its  $\Delta G^\circ_{\text{rxn}}$  by 2.



Lastly, rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest.  $\Delta G^\circ_{\text{rxn}}$  for the reaction of interest is then the sum of the  $\Delta G$ 's for the steps.



## Example 18.9 Calculating $\Delta G^\circ_{\text{rxn}}$ for a Stepwise Reaction

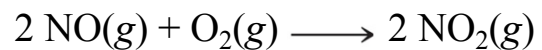
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### For Practice 18.9

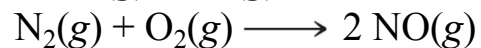
Find  $\Delta G^\circ_{\text{rxn}}$  for the reaction:



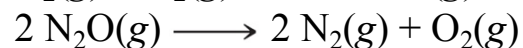
Use the following reactions with known  $\Delta G^\circ_{\text{rxn}}$  values:



$$\Delta G^\circ_{\text{rxn}} = -71.2 \text{ kJ}$$

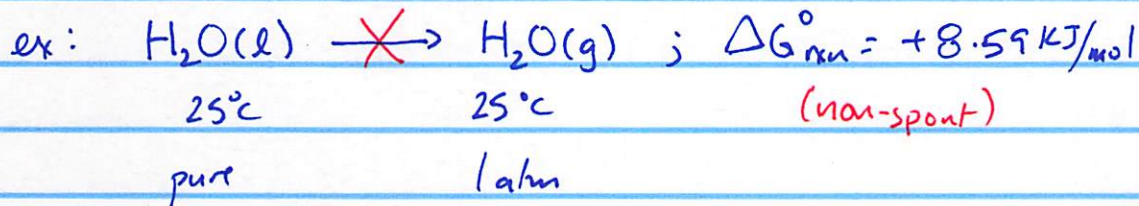


$$\Delta G^\circ_{\text{rxn}} = +175.2 \text{ kJ}$$



$$\Delta G^\circ_{\text{rxn}} = -207.4 \text{ kJ}$$

$\Delta G_{rxn}$  vs.  $\Delta G_{rxn}^\circ$   
 non-STD conditions vs. STD conditions  
 gas: 1 atm  
 s/l: pure  
 (aq): 1M



Doesn't water evaporate?  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$   
 yes ... but water vapor  $\neq$  1 atm!  
 vp of  $\text{H}_2\text{O}$  @ 25°C < 1 atm.

Can calculate  $\Delta G$  under non-std. conditions using:

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

8.3145 J/mol·K      temp (K)      rxn quotient

lower than vp.  
↓

What's  $\Delta G$  for:  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}, 0.010 \text{ atm})$  ?  
25°C

$$Q = \frac{P_{\text{H}_2\text{O}}}{1} = P_{\text{H}_2\text{O}} = 0.010$$

$$\Delta G = \Delta G^\circ + RT \ln Q = +8.59 \frac{\text{kJ}}{\text{mol}} + 8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times 298.15 \text{ K} \times$$

$$\ln(0.010) \times \frac{\text{kJ}}{10^3 \text{ J}}$$

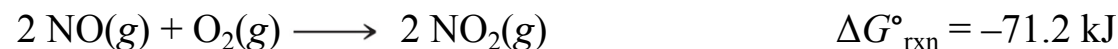
$$\Delta G = +8.59 \frac{\text{kJ}}{\text{mol}} + (-11.4 \text{ kJ/mol})$$

$$= -2.81 \text{ kJ/mol}, \text{ so... yes, it's spent!}$$

See ex: 18.10, p 872 for another problem...

## Example 18.10 Calculating $\Delta G^\circ_{\text{rxn}}$ under Nonstandard Conditions

Consider the reaction at 298 K:



Calculate  $\Delta G_{\text{rxn}}$  under these conditions:

$$P_{\text{NO}} = 0.100 \text{ atm}; \quad P_{\text{O}_2} = 0.100 \text{ atm}; \quad P_{\text{NO}_2} = 2.00 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?

### Solution

Use the law of mass action to calculate  $Q$ .

$$Q = \frac{(P_{\text{NO}_2})^2}{(P_{\text{NO}})^2 P_{\text{O}_2}} = \frac{(2.00)^2}{(0.100)^2(0.100)} = 4.00 \times 10^3$$

Substitute  $Q$ ,  $T$ , and  $\Delta G^\circ_{\text{rxn}}$  into Equation 18.13 to calculate  $\Delta G_{\text{rxn}}$ . (Since the units of  $R$  include joules, write  $\Delta G^\circ_{\text{rxn}}$  in joules.)

$$\begin{aligned} \Delta G_{\text{rxn}} &= \Delta G^\circ_{\text{rxn}} + RT \ln Q \\ &= -71.2 \times 10^3 \text{ J} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln(4.00 \times 10^3) \\ &= -71.2 \times 10^3 \text{ J} + 20.5 \times 10^3 \text{ J} \\ &= -50.7 \times 10^3 \text{ J} \\ &= -50.7 \text{ kJ} \end{aligned}$$

The reaction is spontaneous under these conditions, but less spontaneous than it would be under standard conditions (because  $\Delta G_{\text{rxn}}$  is less negative than  $\Delta G^\circ_{\text{rxn}}$ ).

## Example 18.10 Calculating $\Delta G^\circ_{\text{rxn}}$ under Nonstandard Conditions

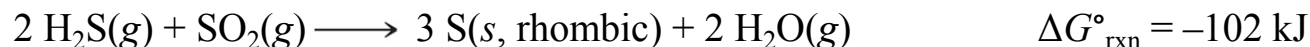
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### Check

The calculated result is consistent with what you would expect based on Le Châtelier's principle; increasing the concentration of the products and decreasing the concentration of the reactants relative to standard conditions should make the reaction less spontaneous than it was under standard conditions.

### For Practice 18.10

Consider the reaction at 298 K:



Calculate  $\Delta G_{\text{rxn}}$  under these conditions:

$$P_{\text{H}_2\text{S}} = 2.00 \text{ atm}; \quad P_{\text{SO}_2} = 1.50 \text{ atm}; \quad P_{\text{H}_2\text{O}} = 0.0100 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?

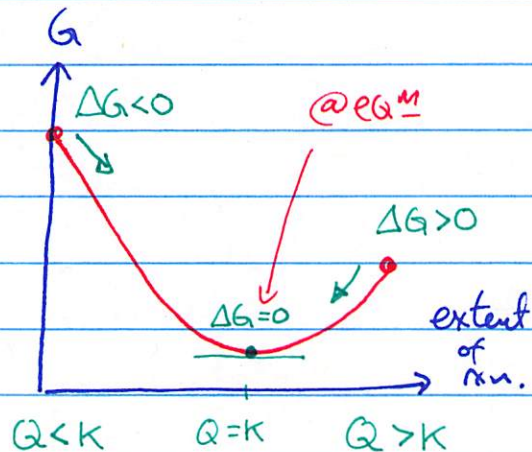


## Relating $\Delta G_{rxn}$ to $K$

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

@ eqm,  $K = Q$   
 $\Delta G = 0$

@ eqm

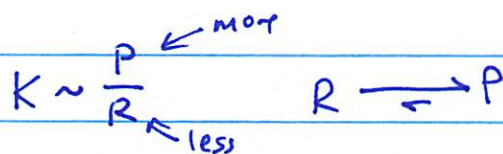


$$0 = \Delta G^\circ + RT \ln K$$

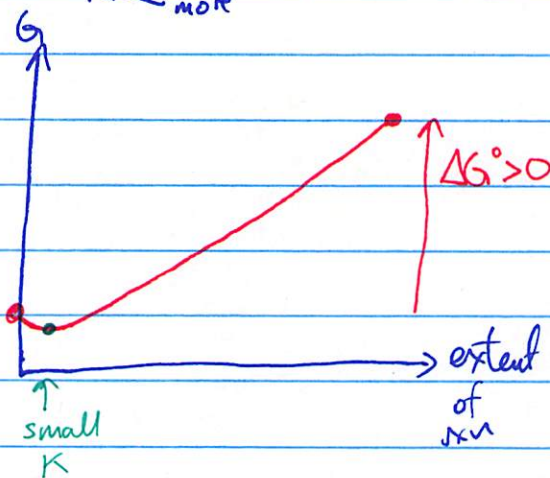
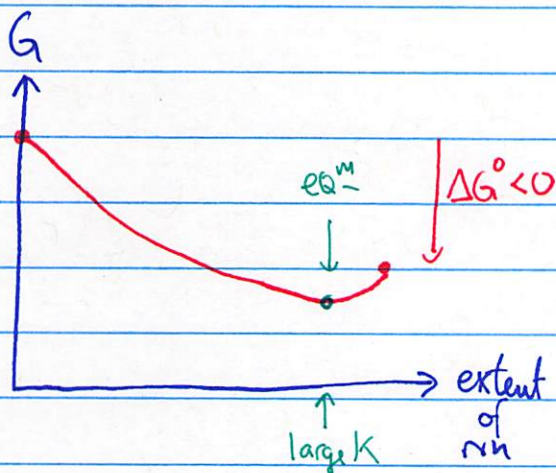
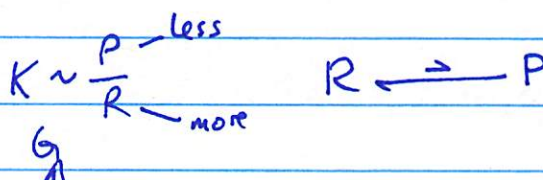
$$\Rightarrow \Delta G^\circ = -RT \ln K$$

rearrange:  $\ln K = \frac{-\Delta G^\circ}{RT} \Rightarrow K = e^{\frac{-\Delta G^\circ}{RT}}$

So, if  $\Delta G^\circ < 0$ ,  $K > 1$



$\Delta G^\circ > 0$ ,  $K < 1$



Ala-Gly rxn:  $\Delta G_{\text{rxn}}^{\circ} = +29 \text{ kJ/mol}$  @  $37^{\circ}\text{C}$

$$K = e^{-\Delta G^{\circ}/RT}$$

$$= e^{\frac{-29,000 \text{ J/mol}}{8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times 310. \text{K}}} = e^{-11.25}$$
$$= 1.3 \times 10^{-5}$$

but, coupled w/ ATP hydrolysis,  $\Delta G^{\circ} = -21 \text{ kJ/mol}$

$$K = e^{\frac{-21,000 \text{ J/mol}}{RT}} = 2.2$$

million times  
more  
favorable

## Ch 19: Electrochemistry

Redox rxns: ox (loss  $e^{-}$ )  $\xrightarrow{e^{-} \text{ flow}}$  red (gain  $e^{-}$ )  
... voltage (diff'ce in E)  
... electricity.