

CHEMISTRY 104 – Help Sheet #17

Thermodynamics – Part II

Do the topics appropriate for your course

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<https://clc.chem.wisc.edu/> (Resource page)

Nuggets: Free Energy (ΔG and ΔG°); Spontaneous Reactions; Calculating K from $\Delta_r G^\circ$; T when a reaction is spontaneous; Van't Hoff equation/graph; Extent of reaction graph

FREE ENERGY (G): a value that relates the change in enthalpy, ΔH , and entropy, ΔS , at a given T:

$$G \equiv H - TS; \Delta_r G = \Delta_r H - T\Delta_r S$$

free energy represents the maximum amount of non-expansion useful work that can be obtained from a system at constant T and P; reactions will be driven to the side which lowers the overall free energy of the system

$\Delta_r G > 0$ (+) \rightarrow *non-spontaneous reaction in the forward direction; reactants are favored (endergonic)*

$\Delta_r G < 0$ (-) \rightarrow *spontaneous reaction in the forward direction; products are favored (exergonic)*

Units of $\Delta_r G = \text{kJ/mol}$

Calculations involving ΔG (Units of $\Delta_r G = \text{kJ/mol}$):

$$\Delta_r G^\circ = \sum(n_p)\Delta_f G^\circ_{\text{products}} - \sum(n_r)\Delta_f G^\circ_{\text{reactants}}$$

where $\Delta_f G^\circ$ = free energy of formation; n_p = #mol product; n_r = #mol reactant;

$\Delta_f G^\circ = 0$ for all elements in their standard state (e.g., $\Delta_f G^\circ = 0$ for $\text{O}_2(\text{g})$)

Standard States: $\text{F}_2(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$; $\text{Br}_2(\text{l})$, $\text{Hg}(\text{l})$; $\text{I}_2(\text{s})$, $\text{C}_{\text{graphite}}(\text{s})$, $\text{S}_8(\text{s})$, $\text{P}_4(\text{s})$; other elements are solids and monoatomic

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \quad (T \text{ in K})$$

Note: $\Delta_r S^\circ$ has units of J/K; $\Delta_r H^\circ$ and $\Delta_r G^\circ$ usually have units of kJ/mol; be careful with units!

$\Delta_r G = \Delta_r G^\circ + (RT)\ln Q$ used for *non-standard conditions* when the system is *not* at equilibrium;

Q is reaction quotient; T in K; R = 8.314 J/K mol

at equilibrium $\Rightarrow \Delta_r G = 0$; $Q \rightarrow K$; $\Delta_r G^\circ \neq 0$ and the equation simplifies to:

$$\Delta_r G^\circ = -RT\ln K \quad \text{and} \quad K = e^{-\Delta_r G^\circ/RT}$$

(Notation: $\Delta_{\text{sys}}G$ where "sys" = system" and is understood to be equivalent to $\Delta_r G$, where "r" = reaction)

DERIVING ΔG° from ΔS° and ΔH°

Start with: $\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{surr}} + \Delta S^\circ_{\text{sys}}$

Make a substitution for $\Delta S^\circ_{\text{surr}}$ using: $\Delta S^\circ_{\text{surr}} = q_{\text{surr}}/T$; since $q_{\text{surr}} = -q_{\text{sys}}$ then

$\Delta S^\circ_{\text{surr}} = -q_{\text{sys}}/T$; at constant P: $\Delta H^\circ = q_p = q_{\text{sys}}$ then:

$\Delta S^\circ_{\text{surr}} = -\Delta H^\circ_{\text{sys}}/T$ subbing this into the equation yields:

$$\Rightarrow \Delta S^\circ_{\text{univ}} = -\Delta H^\circ_{\text{sys}}/T + \Delta S^\circ_{\text{sys}}$$

now multiply the equation by (-T) and the equation becomes:

$\Rightarrow -T\Delta S^\circ_{\text{univ}} = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$ we define $\Delta G^\circ_{\text{sys}} = -T\Delta S^\circ_{\text{univ}}$ and the equation becomes:

$$\Rightarrow \Delta G^\circ_{\text{sys}} = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}} \quad (\text{often written as: } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ)$$

Example 1: Calculate $\Delta_r G^\circ$ for the reaction: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ given

$$\Delta_f G^\circ_{\text{CH}_4(\text{g})} = -50.7\text{kJ/mol}; \Delta_f G^\circ_{\text{CO}_2(\text{g})} = -394.4\text{kJ/mol}; \Delta_f G^\circ_{\text{H}_2\text{O}(\text{g})} = -228.6\text{kJ/mol}$$

Answer 1: **-800.9kJ/mol** { $\Delta_r G^\circ = \sum(n_p)\Delta_f G^\circ_{\text{products}} - \sum(n_r)\Delta_f G^\circ_{\text{reactants}}$; $\Delta_r G^\circ = [1(-394.4) + 2(-228.6)] - [1(-50.7) + 2(0)] = -800.9\text{kJ/mol}$ }

Example 2: Calculate $\Delta_r G^\circ$ for the reaction: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ given

$$\Delta_f H^\circ = -802.3 \text{ kJ/mol}; \Delta_f S^\circ = -5.2 \text{ J/molK (these values were calculated on HelpSheet \#16 in examples 3 and 6)}$$

Answer 2: -800.7 kJ/mol $\{\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ; \Delta_r G^\circ = -802.3 \text{ kJ/mol} - (298.15 \text{ K})(-5.2 \text{ J/molK})(1 \text{ kJ}/1000 \text{ J}) = -800.7 \text{ kJ/mol}\}$
(difference from answer in Example 1 above is rounding differences)

Example 3: Calculate K for the reaction: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ given $\Delta_r G^\circ = -800.8 \text{ kJ/mol}$

Answer 3: $K = e^{323} = 2.1 \times 10^{140}$ $\{\Delta_r G^\circ = -RT \ln K; -800.8 \text{ kJ/mol}(1000 \text{ J/kJ}) = -(8.314 \text{ J/molK})(298.15 \text{ K}) \ln K; \ln K = 323.1; K = e^{323.1} = 2.1 \times 10^{140}\}$
 $\{K = e^{323.1} = 2.09 \times 10^{140}$; this calculation is too large for some calculators so just leave it as $K = e^{323}\}$

Example 4: The acid dissociation reaction, $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$, has a $K_a = 1.8 \times 10^{-5}$ at 25°C .

- At equilibrium what is the value of $\Delta_r G^\circ$?
- Using the value of $\Delta_r G^\circ$ just calculated, determine the value of ΔG if $[\text{CH}_3\text{COOH}] = 1.00 \text{ M}$, $[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+] = 0.20 \text{ M}$.
- Based on the value of ΔG from part b, is the reaction spontaneous under these conditions?
- Based on a comparison between Q and K_a , which way will the reaction shift?

Answer 4: a. 27.1 kJ/mol $\{\text{use } \Delta G^\circ = -RT \ln K = -8.314(298) \ln(1.8 \times 10^{-5}) = 27,081 \text{ J/mol} = 27.1 \text{ kJ/mol}\}$

(Note: $\Delta_r G^\circ$ can also be calculated from $\Delta_r G^\circ = \sum(n_p)\Delta_f G^\circ_{\text{products}} - \sum(n_r)\Delta_f G^\circ_{\text{reactants}}$ though values in a table are needed; here are the results: $\Delta_r G^\circ = [1(\Delta_f G^\circ_{\text{CH}_3\text{COO}^-} + 1(\Delta_f G^\circ_{\text{H}^+})] - [1(\Delta_f G^\circ_{\text{CH}_3\text{COOH}})]$; $\Delta_r G^\circ = [1(-369.31) + 1(0)] - [1(-396.46)] = 27.15 \text{ kJ/mol}$

b. **19.1 kJ/mol** $\{\text{use } \Delta_r G = \Delta G^\circ + RT \ln Q; Q = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}; \Delta G = 27,081 + (8.314)(298) \ln \frac{(0.20)(0.20)}{1.0}$;

$$\Delta_r G = 27,081 + (8.314)(298)(-3.219) = 19,102 \text{ J/mol}; \Delta_r G = 19.1 \text{ kJ/mol}\}$$

c. **Non-spontaneous** to the product side because $\Delta_r G > 0$

d. **Shift left** to reactant-side $\{Q = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}; Q = \frac{(0.20)(0.20)}{(1.0)} = 0.040$; since $Q > K$, the reaction shifts left to the reactant side}

MANIPULATING ΔH , ΔS , and ΔG AS THE REACTION IS CHANGED

- Reverse reaction:** change the sign: $\Delta_r X_{\text{forward}} \Rightarrow -\Delta_r X_{\text{reverse}}$
- Multiply** the coefficients of a reaction by a constant, c: $\Delta_r X_{\text{new}} \Rightarrow (c)\Delta_r X$
- Add** reactions: $\Delta_r X_{\text{net}} = \Delta_r X_1 + \Delta_r X_2 + \dots$

WHEN IS A REACTION SPONTANEOUS

Case	ΔH°	description	ΔS°	description	ΔG°	Spontaneous
1	-	exothermic	+	more random/disordered	-	yes; always spontaneous
2	-	exothermic	-	less random/more ordered	- or +	depends on T, ΔH° , and ΔS° values; spontaneous to products at low T (enthalpy driven)
3	+	endothermic	+	more random/disordered	- or +	depends on T, ΔH° , and ΔS° values; spontaneous to products at high T (entropy driven)
4	+	endothermic	-	less random/more ordered	+	no; never spontaneous

In cases 2 and 3 above where the sign of $\Delta_r G^\circ$ depends on T, the value of T can be calculated by setting $\Delta_r G^\circ = 0$. The sign of $\Delta_r G^\circ$ changes from + to - at this point, and T can then be determined as follows:

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

$$0 = \Delta_r H^\circ - T\Delta_r S^\circ \quad (\text{setting } \Delta_r G^\circ = 0 \text{ because it goes from + to - at this point})$$

$$T\Delta_r S^\circ = \Delta_r H^\circ \quad (\text{rearranging})$$

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} \quad \text{this is } T \text{ when a reaction becomes spontaneous/nonspontaneous; it is when } \Delta_r G^\circ = 0$$

Example 5: I. For the endothermic reaction: $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ which statement is correct?

- a. $\Delta_r H^\circ > 0, \Delta_r S^\circ > 0$ b. $\Delta_r H^\circ < 0, \Delta_r S^\circ < 0$ c. $\Delta_r H^\circ > 0, \Delta_r S^\circ < 0$ d. $\Delta_r H^\circ < 0, \Delta_r S^\circ > 0$

II. What is the sign of ΔG° ? Specify positive, negative, or spontaneous (-) at low T or spontaneous (-) at high T.

III. If $\Delta_r H^\circ = 197.8\text{kJ}$ and $\Delta_r S^\circ = 188.1\text{J/K}$, at what temperatures would this reaction be spontaneous?

Answer 5: I. a {since this is an endothermic reaction $\rightarrow \Delta_r H^\circ > 0$; going from 2 gaseous particles \rightarrow 3 gas particles $\rightarrow \Delta_r S^\circ > 0$ }

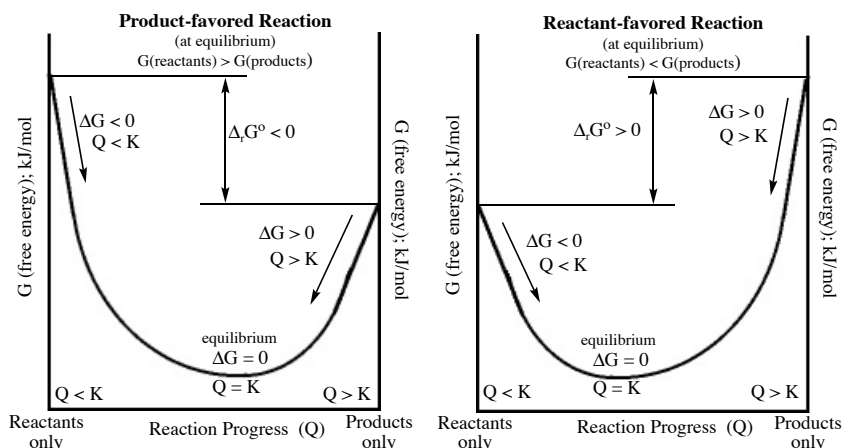
II. Spontaneous at high T {since $\Delta_r H^\circ > 0$ (+) and $\Delta_r S^\circ > 0$ (+) this reaction will be spontaneous at high T}

III. $T > 1052\text{K}$ {For reaction to be spontaneous towards products: $\Delta_r G^\circ < 0$; $T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ}$; $T = \frac{197.8\text{kJ}(1000\text{J}/\text{kJ})}{188.1\text{J/K}}$; $T = 1052\text{K}$;

since from Part II the reaction is spontaneous at high T this means at temperatures above 1052K the reaction is spontaneous}

G versus Extent of Reaction

The diagram (near right) shows the progress of a **product-favored reaction** versus G (note that the low point where $\Delta G = 0$ is closer to the all-product side; products favored.). At the all-reactant side (left vertical axis) or all-product side (right vertical axis), the system is at standard state and the difference between the left and right sides = ΔG° . At the far left where only reactants exist, the reaction will go to the right spontaneously ($Q < K$), the shift will decrease G_{sys} , and this direction is downhill as products form. If the reaction started at the far right where only products existed, the reaction will go to the left spontaneously ($Q > K$), the shift will decrease G_{sys} , and this direction is downhill as reactants form. At the lowest point, $\Delta G = 0$, the system is at equilibrium, $Q = K$, and there is no longer a driving force to shift.



The diagram at the far right is the same diagram but it is for a **reactant-favored reaction** (note that the low point where $\Delta G = 0$ is closer to the all-reactant side; reactants favored.)

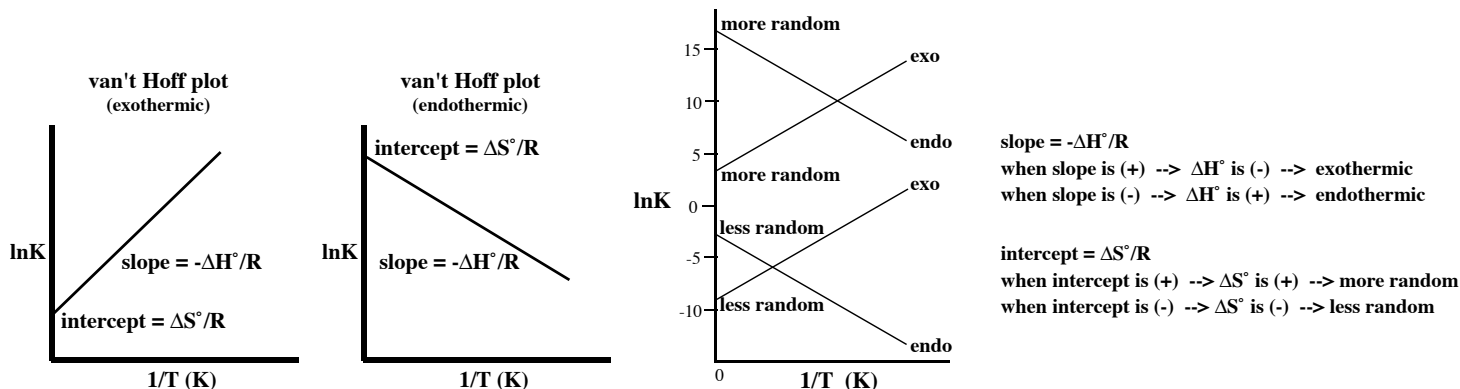
$$\text{Van't HOFF EQUATION: } \ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

this is an equation of a line, $y = mx + b$ with

$y = \ln K$; $x = 1/T$, and slope = $m = -(\Delta H^\circ/R)$; y-intercept = $b = \Delta S^\circ/R$

$R = 8.314 \text{ J/molK}$; ΔH° and ΔS° need to be in J (ΔH° often given in kJ)

Since ΔH° can be (-) or (+) \rightarrow the slope can be (-) or (+)



Example 7: The reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, was studied at several temperatures

and a plot of $\ln K_{eq}$ versus $1/T$ was generated.

- What is the value of $\Delta_r S^\circ$?
- What is the value of $\Delta_r H^\circ$?
- What is the value of $\Delta_r G^\circ$ at $25^\circ C$?
- What is the value of K at $1000^\circ C$?

Answer 7:

- 171J/molK** {from the equation, $\ln K = \left(\frac{-\Delta_r H^\circ}{R}\right)\left(\frac{1}{T}\right) + \left(\frac{\Delta_r S^\circ}{R}\right)$, the

$$y\text{-intercept} = (\Delta_r S^\circ / R) \text{ where } R = 8.314 \text{ J/molK. Therefore, } -20.592 = \frac{\Delta_r S^\circ}{8.314};$$

$$\Delta_r S^\circ = (-20.592)(8.314) = -171.2 \text{ J/molK}$$

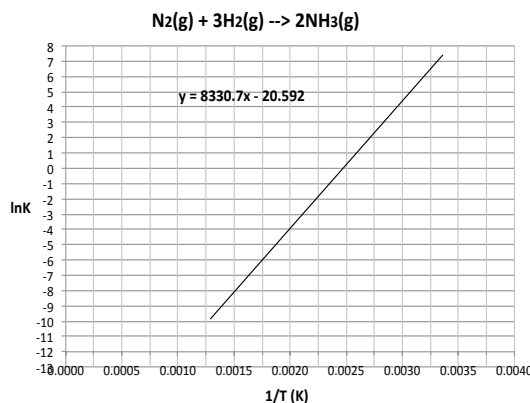
- 69.3kJ/mol** {from the equation, $\ln K = \left(\frac{-\Delta_r H^\circ}{R}\right)\left(\frac{1}{T}\right) + \left(\frac{\Delta_r S^\circ}{R}\right)$, the slope = $-(\Delta_r H^\circ / R)$ where

$$R = 8.314 \text{ J/molK. Therefore, } 330.7 = \frac{-\Delta_r H^\circ}{8.314}; \Delta_r H^\circ = -(8330.7)(8.314) = -69,261 \text{ J/mol} = -69.3 \text{ kJ/mol}$$

- 18.3kJ/mol** $\{\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ; \Delta_r G^\circ = (-69,300 \text{ J/mol}) - (25+273 \text{ K})(-171 \text{ J/(mol K)}) = -18342 \text{ J/mol} = -18.3 \text{ kJ/mol}\}$

- 7.93×10^{-7}** {use the equation, $y = 8330.7x - 20.593$ where $y = \ln K$ and $x = 1/T$; $\ln K$ at $1000^\circ C$: $\ln K = (8330.7)\left(\frac{1}{1000 + 273}\right) - 20.592$;

$$\ln K = 6.544 - 20.592; \ln K = -14.05; K = e^{-14.05} = 7.927 \times 10^{-7}$$



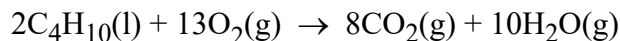
Summary of Equations

$\Delta H^\circ_{rxn} = \sum \Delta_f H^\circ_{prod}(n_{prod}) - \sum \Delta_f H^\circ_{react}(n_{react})$	$\Delta S^\circ_{univ} = \Delta S^\circ_{surr} + \Delta S^\circ_{sys}$	$\Delta G^\circ_{rxn} = \sum \Delta_f G^\circ_{prod}(n_{prod}) - \sum \Delta_f G^\circ_{react}(n_{react})$
$\Delta S^\circ_{rxn} = \sum S^\circ_{prod}(n_{prod}) - \sum S^\circ_{react}(n_{react})$	$\Delta S^\circ_{surr} = \frac{\Delta H^\circ_{surr}}{T_{surr}} = \frac{-\Delta H^\circ_{sys}}{T_{surr}}$	$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$
$\Delta G^\circ_{rxn} = \sum \Delta_f G^\circ_{prod}(n_{prod}) - \sum \Delta_f G^\circ_{react}(n_{react})$	$\Delta S^\circ_{sys} = \frac{q_{rev}}{T_{sys}} = \frac{\Delta H^\circ_{sys}}{T_{sys}}$	$T_{spontaneous} = \frac{\Delta H^\circ_{rxn}}{\Delta S^\circ_{rxn}}$
$\ln K = \left(\frac{-\Delta_r H^\circ}{R}\right)\frac{1}{T} + \left(\frac{\Delta_r S^\circ}{R}\right)$ (Van't Hoff)	$\Delta S^\circ_{univ} = \frac{-\Delta H^\circ_{sys}}{T_{surr}} + \frac{\Delta H^\circ_{sys}}{T_{sys}}$	$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q$
$T_{(mp \text{ or } bp)} = \frac{q_{rev}}{\Delta S^\circ_{rxn}} = \frac{\Delta H^\circ_{rxn}}{\Delta S^\circ_{rxn}}$	$S = k \ln W$; $\Delta S = k \ln \left(\frac{W_{final}}{W_{initial}}\right)$	$\Delta G^\circ_{rxn} = -RT \ln K$

I. When water freezes at $-10^\circ C$ what are the signs of ΔH° , ΔS° , and ΔG° ? (Assume 1 atm.)

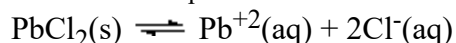
- $\Delta H^\circ < 0, \Delta S^\circ < 0, \Delta G^\circ < 0$
- $\Delta H^\circ > 0, \Delta S^\circ < 0, \Delta G^\circ < 0$
- $\Delta H^\circ < 0, \Delta S^\circ > 0, \Delta G^\circ > 0$
- $\Delta H^\circ > 0, \Delta S^\circ > 0, \Delta G^\circ < 0$
- $\Delta H^\circ < 0, \Delta S^\circ < 0, \Delta G^\circ > 0$

II. For the reaction below, predict the signs of ΔH° , ΔS° , and ΔG° .



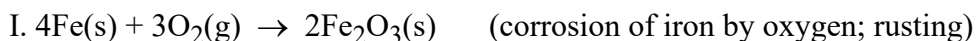
- $\Delta H^\circ > 0; \Delta S^\circ > 0; \Delta G^\circ < 0$
- $\Delta H^\circ > 0; \Delta S^\circ < 0; \Delta G^\circ > 0$
- $\Delta H^\circ < 0; \Delta S^\circ > 0; \Delta G^\circ < 0$
- $\Delta H^\circ < 0; \Delta S^\circ < 0; \Delta G^\circ > 0$
- $\Delta H^\circ < 0; \Delta S^\circ > 0; \Delta G^\circ > 0$

III. $PbCl_2(s)$ has a K_{sp} of 1.6×10^{-5} at $25.0^\circ C$. Select which answer below is **correct** for the reaction:

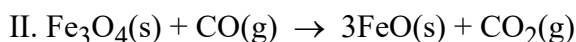


- $\Delta H^\circ > 0, \Delta S^\circ > 0, \Delta G^\circ > 0$
- $\Delta H^\circ > 0, \Delta S^\circ > 0, \Delta G^\circ < 0$
- $\Delta H^\circ < 0, \Delta S^\circ < 0, \Delta G^\circ > 0$
- $\Delta H^\circ < 0, \Delta S^\circ < 0, \Delta G^\circ < 0$
- $\Delta H^\circ < 0, \Delta S^\circ > 0, \Delta G^\circ > 0$
- $\Delta H^\circ > 0, \Delta S^\circ < 0, \Delta G^\circ < 0$

2. For the two reactions below, calculate $\Delta_r S^\circ$ and $\Delta_r H^\circ$ using the standard thermodynamic values listed. From these values, then determine $\Delta_r G^\circ$ and determine whether the reaction is spontaneous.



	Fe(s)	O ₂ (g)	Fe ₂ O ₃ (s)
S° (J/mol K)	27.3	205.1	87.4
$\Delta_f H^\circ$ (kJ/mol)			-824.2



	Fe ₃ O ₄ (s)	CO(g)	FeO(s)	CO ₂ (g)
S° (J/mol K)	146.4	197.7	57.5	213.7
$\Delta_f H^\circ$ (kJ/mol)	-1118.4	-110.5	-266.3	-393.5

3. $\Delta_r G^\circ$ for the reaction is 7.0kJ.

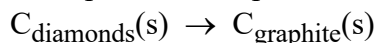


Given $\Delta_f G^\circ$ of Al₂O₃(s) = -1582kJ/mol and $\Delta_f G^\circ$ of H₂O(g) = -229kJ/mol, calculate $\Delta_f G^\circ$ of Al(OH)₃(s).

4. Which reaction represents the standard free energy of formation, $\Delta_f G^\circ$, for CaCO₃(s)?

- $\text{Ca(s)} + \text{C}_{\text{graphite}}\text{(s)} + 3\text{O(g)} \rightarrow \text{CaCO}_3\text{(s)}$
- $\text{Ca}^{+2}\text{(aq)} + \text{CO}_3^{-2}\text{(aq)} \rightarrow \text{CaCO}_3\text{(s)}$
- $\text{Ca}^{+2}\text{(aq)} + \text{C}^{+4}\text{(aq)} + 3\text{O}^{-2}\text{(aq)} \rightarrow \text{CaCO}_3\text{(s)}$
- $\text{Ca(s)} + \text{C}_{\text{graphite}}\text{(s)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{CaCO}_3\text{(s)}$
- $2\text{Ca(s)} + 2\text{C}_{\text{graphite}}\text{(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CaCO}_3\text{(s)}$

5. a. Using the $\Delta_f G^\circ = 2.9\text{kJ/mol}$ for C_{diamond}(s), determine $\Delta_r G^\circ$ for the process of diamonds turning into graphite at room temperature and pressure.



b. The $\Delta_r G^\circ$ just calculated should be less than zero and therefore the reaction is spontaneous. Give an explanation why this process even though it is spontaneous, doesn't seem to happen in real life.

6. Given the reaction, $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$, and data shown answer the questions below.

$$\Delta_f G^\circ = -95.3\text{kJ/mol}; \Delta_r H^\circ = -184.6\text{kJ}; \Delta_r S^\circ = 20.0\text{J/K}$$

- From the above data, $\Delta_r G^\circ$ can be calculated in two ways. Calculate $\Delta_r G^\circ$ at 25.0°C using $\Delta_f G^\circ$ values and also calculate it using $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values.
- Is this reaction spontaneous in the forward direction at 25°C?
- Calculate $\Delta_r G^\circ$ at 150°C assuming $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ are constant as temperature changes.
- Calculate K at 25.0°C.

7. For 1.00mol CH₃OH(s), the $\Delta H_{\text{fusion}} = 3.18\text{kJ/mol}$ and $\Delta S^\circ = 18.1\text{J/K}$; at what temperature in °C does CH₃OH(s) melt?

8. Given the exothermic reaction of iron rusting, $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$, which state is **true**?

- The reaction will always be spontaneous.
- The reaction will never be spontaneous.
- The reaction will be spontaneous when T is high.
- The reaction will be spontaneous when T is low.
- One must consider kinetics to answer this question.

9. Given the following reaction, $4\text{NH}_3\text{(g)} + 7\text{O}_2\text{(g)} \rightarrow 4\text{NO}_2\text{(g)} + 6\text{H}_2\text{O(g)}$ and the data listed complete the following calculations.

	$\text{NH}_3\text{(g)}$	$\text{O}_2\text{(g)}$	$\text{NO}_2\text{(g)}$	$\text{H}_2\text{O(g)}$
S° (J/mol K)	192.5	205.1	240.1	188.8
$\Delta_f H^\circ$ (kJ/mol)	-46.1		33.2	-241.8
$\Delta_f G^\circ$ (kJ/mol)	16.5		51.3	-228.6

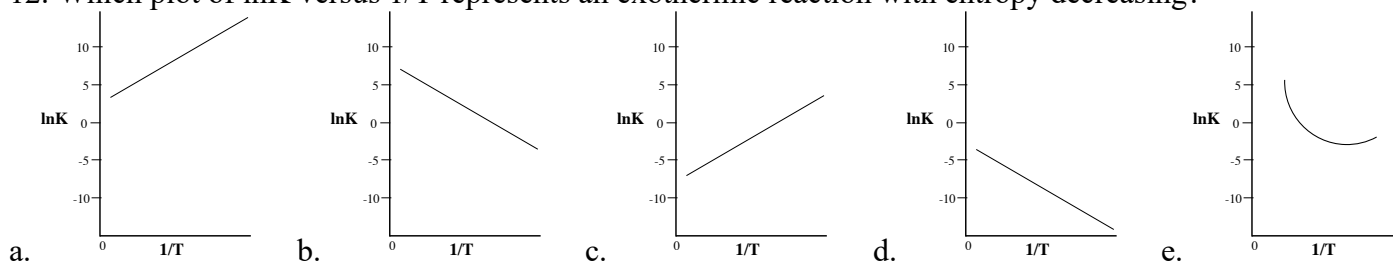
- Calculate $\Delta_r S^\circ$ at 25.0°C .
- Calculate $\Delta_r H^\circ$ at 25.0°C .
- Calculate $\Delta_r G^\circ$ at 25.0°C .
- Is this reaction spontaneous at 25.0°C ?

10. If a reaction has $\Delta_r H^\circ = -125\text{kJ}$ and $\Delta_r S^\circ = -250\text{J/K}$, at what T will the reaction be spontaneous towards the products?

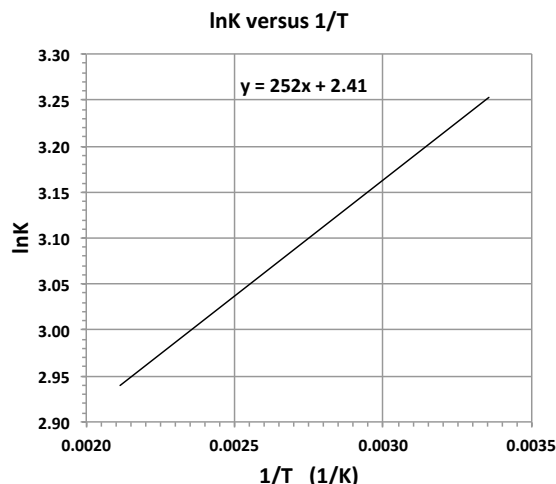
- When $T = 500\text{K}$
- When T is less than 500K
- When T is greater than 500K
- When T is less than 0.5K
- This reaction will never be spontaneous.

11. If $\Delta G^\circ = 22.4\text{kJ/mol}$ at 25°C for the reaction: $\text{C}_6\text{H}_5\text{COOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^-\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)}$, what is the K_a value for this reaction?

12. Which plot of $\ln K$ versus $1/T$ represents an exothermic reaction with entropy decreasing?



13. Use the Van't Hoff plot below to answer the following questions.



- What is the value of ΔS° ?
- What is the value of ΔH° ?
- What is the value of K at 60.0°C ?
- What is the value of K at -15.0°C ?

14. For the reaction $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$, the K_a is 7.4×10^{-4} .

- Calculate ΔG for the reaction at 25.0°C if a solution contains $[\text{HNO}_2] = 0.550\text{M}$, $[\text{NO}_2^-] = 0.250\text{M}$, and has a $\text{pH} = 2.50$.
- Is this reaction spontaneous towards the products or spontaneous towards the reactants?

15. Calculate ΔG at 25.0°C for the reaction: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ with $\Delta_f G^\circ_{\text{NO}} = 86.55\text{kJ/mol}$ and $\Delta_f G^\circ_{\text{NO}_2} = 51.31\text{kJ/mol}$ and the partial pressures $\text{NO} = 2.00\text{atm}$, $\text{O}_2 = 0.015\text{atm}$, and $\text{NO}_2 = 0.039\text{atm}$.

16. For the reaction $\text{Ag}_3\text{PO}_4(\text{s}) \rightleftharpoons 3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$, the K_{sp} is 1.4×10^{-16} .

- Calculate ΔG for the reaction at 25.0°C if a solution contains $\text{Ag}_3\text{PO}_4(\text{s})$ with $[\text{Ag}^+] = 1.5 \times 10^{-5}\text{M}$ and $[\text{PO}_4^{3-}] = 4.0 \times 10^{-3}\text{M}$.
- Is this reaction spontaneous towards the products or spontaneous towards the reactants?
- Will some Ag_3PO_4 precipitate or will some of it dissolve?

ANSWERS

- I. a {g \rightarrow l \rightarrow s are exothermic processes $\rightarrow \Delta H^\circ < 0$; going from a solid \rightarrow liquid \rightarrow entropy decreases $\rightarrow \Delta S^\circ < 0$; since water freezes spontaneously at $-10^\circ\text{C} \rightarrow \Delta G^\circ < 0$ }
- II. c {This is a combustion reaction and therefore exothermic so $\Delta H^\circ < 0$; the reaction goes from 13mol of gas to 18mol of gas so $\Delta S > 0$; from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, if $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$, then $\Delta G^\circ < 0$ }
- III. a {since the $K \ll 1$, this implies the reaction is reactant-favored and therefore $\Delta G^\circ > 0$; the reaction has increasing entropy, ΔS° , as the solid dissolves into water and therefore $\Delta S^\circ > 0$; since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, and since $\Delta G^\circ > 0$ (+) and $\Delta S^\circ > 0$ (+), ΔH° must be positive; this can also be seen by plugging in the signs into $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ as follows: (+) = $\Delta H^\circ + (-)$; if ΔH° was negative, $\Delta H^\circ < 0$, (+) = (-) + (-) then ΔG° would be negative and $K > 1$ which is not the case}

2. I. $\Delta_r S^\circ = -549.7 \text{ J/K}$; $\Delta_r H^\circ = -1648.4 \text{ kJ}$; $\Delta_r G^\circ = -1484.5 \text{ kJ}$; spontaneous

$$\{\text{use: } \Delta S^\circ_{\text{sys}} = \Sigma(n_p)S^\circ_{\text{products}} - \Sigma(n_r)S^\circ_{\text{reactants}}; \Delta_r S^\circ = [2(S^\circ_{\text{Fe}_2\text{O}_3})] - [4(S^\circ_{\text{Fe}}) + 3(S^\circ_{\text{O}_2})];$$

$$\Delta_r S^\circ = [2(87.4)] - [4(27.3) + 3(205.1)] = -549.7 \text{ J/K};$$

$$\text{use: } \Delta H^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f H^\circ_{\text{products}} - \Sigma(n_r)\Delta_f H^\circ_{\text{reactants}}; \Delta_r H^\circ = [2(\Delta_f H^\circ_{\text{Fe}_2\text{O}_3})] - [4(\Delta_f H^\circ_{\text{Fe}}) + 3(\Delta_f H^\circ_{\text{O}_2})];$$

$$\Delta H^\circ_{\text{sys}} = [2(-824.2)] - [4(0) + 3(0)] = -1648.4 \text{ kJ};$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -1648.4 - (298.15 \text{ K})(-549.7 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) = -1648.4 + 163.9 = -1484.5 \text{ kJ};$$

since $\Delta_r G^\circ < 0 \rightarrow$ spontaneous}

II. $\Delta_r S^\circ = 42.1 \text{ J/K}$; $\Delta_r H^\circ = 36.5 \text{ kJ}$; $\Delta_r G^\circ = 24.0 \text{ kJ}$; non-spontaneous

$$\{\text{use: } \Delta S^\circ_{\text{sys}} = \Sigma(n_p)S^\circ_{\text{products}} - \Sigma(n_r)S^\circ_{\text{reactants}}; \Delta_r S^\circ = [3(S^\circ_{\text{FeO}}) + (S^\circ_{\text{CO}_2})] - [(S^\circ_{\text{Fe}_3\text{O}_4}) + (S^\circ_{\text{CO}})]$$

$$\Delta_r S^\circ = [3(57.5) + (213.7)] - [(146.4) + (197.7)] = 42.1 \text{ J/K};$$

$$\text{use: } \Delta H^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f H^\circ_{\text{products}} - \Sigma(n_r)\Delta_f H^\circ_{\text{reactants}}; \Delta_r H^\circ = [3(\Delta_f H^\circ_{\text{FeO}}) + (\Delta_f H^\circ_{\text{CO}_2})] - [(\Delta_f H^\circ_{\text{Fe}_3\text{O}_4}) + (\Delta_f H^\circ_{\text{CO}})];$$

$$\Delta H^\circ_{\text{sys}} = [3(-266.3) + (-393.5)] - [(-1118.4) + (-110.5)] = 36.5 \text{ kJ};$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = 36.5 - (298.15 \text{ K})(42.1 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) = 36.5 - 12.6 = 24.0 \text{ kJ}; \text{ since } \Delta_r G^\circ > 0 \rightarrow \text{non-spontaneous}$$

3. $\Delta_f G^\circ_{\text{Al(OH)}_3(\text{s})} = -1138 \text{ kJ/mol}$ {use: $\Delta G^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f G^\circ_{\text{products}} - \Sigma(n_r)\Delta_f G^\circ_{\text{reactants}}$;

$$\Delta_r G^\circ = [(\Delta_f G^\circ_{\text{Al}_2\text{O}_3}) + 3(\Delta_f G^\circ_{\text{H}_2\text{O}})] - [2(\Delta_f G^\circ_{\text{Al(OH)}_3})]; 7.0 = [(-1582) + 3(-229)] - [2(\Delta_f G^\circ_{\text{Al(OH)}_3})];$$

$$\text{solve for } \Delta_f G^\circ_{\text{Al(OH)}_3}; 7.0 = -2269 - 2(\Delta_f G^\circ_{\text{Al(OH)}_3}) \rightarrow \Delta_f G^\circ_{\text{Al(OH)}_3} = -1138 \text{ kJ/mol}$$

4. d {by definition: should produce 1 mol of substance from its elements in their natural states; “a”: O(g) not natural state; “b”: no ions should be present; “c”: no ions should be present; “e”: should not form 2 mol of product}

5. a. $\Delta G = -2.9 \text{ kJ/mol}$ {use: $\Delta G^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f G^\circ_{\text{products}} - \Sigma(n_r)\Delta_f G^\circ_{\text{reactants}}$;

$$\Delta_r G^\circ = [(\Delta_f G^\circ_{\text{C(graphite)}})] - [(\Delta_f G^\circ_{\text{C(diamond)}})] = [(0)] - [(2.9)] = -2.9 \text{ kJ/mol}$$

b. Even though the reaction is thermodynamically spontaneous it does not proceed spontaneously at room temperature and pressure because of kinetics; that is, it's too slow of a reaction.

6. a. -190.6 kJ {use: $\Delta G^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f G^\circ_{\text{products}} - \Sigma(n_r)\Delta_f G^\circ_{\text{reactants}}$; $\Delta_r G^\circ = [2(\Delta_f G^\circ_{\text{HCl}})] - [(\Delta_f G^\circ_{\text{H}_2}) + (\Delta_f G^\circ_{\text{Cl}_2})]$

$$\Delta_r G^\circ = [2(-95.3)] - [1(0) + 1(0)] = -190.6 \text{ kJ/mol}; \text{ or}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -184,600 - (298.15)(20.0) = -190,563 \text{ J/mol} = -190.6 \text{ kJ/mol}$$

b. yes since $\Delta_r G^\circ < 0$

c. -192.5 kJ { $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -184000 - (150+273)(20) = -192,460 \text{ J/mol} = -192.5 \text{ kJ/mol}$ }

d. $K = 2.5 \times 10^{33}$ { $\Delta_r G^\circ = -RT \ln K$; $-190.6 \text{ kJ/mol} = -(8.314 \text{ J/molK})(298.15 \text{ K}) \ln K$; $\ln K = 76.89$; $K = e^{76.89}$; $K = 2.47 \times 10^{33}$ }

7. -97.5°C { $\Delta S^\circ = \frac{q_{\text{sys}}}{T}$; $\Delta S^\circ = \frac{\Delta H^\circ_{\text{fus}}}{T}$; $T = \frac{\Delta H^\circ_{\text{fus}}}{\Delta S^\circ}$; $T = \frac{(3.18 \text{ kJ})(1000 \text{ J}/1 \text{ kJ})}{18.1 \text{ J/K}} = 175.7 \text{ K}$; $175.7 \text{ K} - 273.15 = -97.5^\circ \text{C}$ }

8. d { ΔS is negative since the reaction takes 4 moles of solid and 3 of gases and reduces that to two moles of solid, entropy is decreasing going from a gas to a solid and going from more moles to fewer moles; ΔH is negative since the reaction is exothermic; to be spontaneous $\Delta_r G$ must be negative; since ΔH is negative and the $-T\Delta S$ is positive, spontaneity will be determined by the relative sizes of these two parts; if $-T\Delta S$ is small then ΔH “wins” and the reaction is spontaneous; for this to occur, T must be small; as T gets higher then $-T\Delta S$ becomes a larger positive value and overwhelms the negative value of ΔH }

9. a. 112.5J/K {use: $\Delta S^\circ_{\text{sys}} = \Sigma(n_p)S^\circ_{\text{products}} - \Sigma(n_r)S^\circ_{\text{reactants}}$; $\Delta_r S^\circ = [4(S^\circ_{\text{NO}_2}) + 6(S^\circ_{\text{H}_2\text{O}})] - [4(S^\circ_{\text{NH}_3}) + 7(S^\circ_{\text{O}_2})]$;
 $\Delta_r S^\circ = [4(240.1) + 6(188.8)] - [4(192.5) + 7(205.1)] = -112.5\text{J/K}$ }
- b. -1133.6kJ {use: $\Delta H^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f H^\circ_{\text{products}} - \Sigma(n_r)\Delta_f H^\circ_{\text{reactants}}$;
 $\Delta_r H^\circ = [4(\Delta_f H^\circ_{\text{NO}_2}) + 6(\Delta_f H^\circ_{\text{H}_2\text{O}})] - [4(\Delta_f H^\circ_{\text{NH}_3}) + 7(\Delta_f H^\circ_{\text{O}_2})] = [4(33.2) + 6(-241.8)] - [4(-46.1) + 7(0)] = -1133.6\text{kJ/mol}$ }
- c. -1100.4kJ {use: $\Delta G^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f G^\circ_{\text{products}} - \Sigma(n_r)\Delta_f G^\circ_{\text{reactants}}$;
 $\Delta_r G^\circ = [4(\Delta_f G^\circ_{\text{NO}_2}) + 6(\Delta_f G^\circ_{\text{H}_2\text{O}})] - [4(\Delta_f G^\circ_{\text{NH}_3}) + 7(\Delta_f G^\circ_{\text{O}_2})] = [4(51.3) + 6(-228.6)] - [4(-16.5) + 7(0)] = -1100.4\text{kJ/mol}$;
or can calculate this by: $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -1,133,600 - (298)(-112.5) = -1,100,075\text{J/mol} = -1101.1\text{kJ/mol}$ }
- d. yes since $\Delta G^\circ < 0$
10. b {for spontaneous reaction $\Delta_r G^\circ < 0$ (-); $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$; set $\Delta_r G^\circ = 0$ and solve for T;
 $0 = -125\text{kJ}(1000\text{J/kJ}) - T(-250\text{J/K})$; $0 = -125000 + 250T$; $T = 125,000/250 = 500\text{K}$; when $T < 500$ the reaction will have a $\Delta_r G^\circ < 0$ and it will be spontaneous}
11. 1.2×10^{-4} { $\Delta G^\circ = -RT\ln K$; $K = e^{-\Delta G^\circ/RT}$; $K = e^{-(-22.4\text{kJ})(1000\text{J/kJ}) / (8.314)(298.15)}$; $K = e^{-22,400/2479} = e^{-9.04}$;
 $K = 1.19 \times 10^{-4}$ }
12. c {from the Van't Hoff equation the slope = $-(\Delta_r H/R)$; for an exothermic reaction $\Delta H < 0$ (-) and the slope > 0 (+); this means either graph "a" or "c" must be the correct choice; from the equation Van't Hoff, the y-intercept = $(\Delta_r S/R)$; for entropy to be decreasing means $\Delta S < 0$ (-) and the y-intercept must be negative; this means graph "c" must be the correct choice}
13. a. 20.0J/K {y-intercept = $\Delta S^\circ/R$; $\Delta S^\circ = (2.41)(8.314) = 20.04\text{J/K}$ }
- b. -2096J/mol {slope = $-\Delta H^\circ/R$; $\Delta H^\circ = -(252)(8.314) = -2095.1\text{J/mol}$ }
- c. 24 { $T = 60+273 = 333$; can use the graph or the equation of the line; from the graph: $1/T = 1/333 = 0.0030$; at that value of x the y value is 3.16; $\ln K = 3.16$; $K = e^{3.16} = 23.6$; using the equation: $y = 252(1/333) + 2.41 = 3.167$; $\ln K = 3.167$;
 $K = e^{3.167} = 23.74$ }
- d. 30. { $T = -15+273 = 258$; $1/T = 1/258 = 0.00388$; cannot use the graph since this x-value is off the graph; use the equation:
 $y = 252(0.00388) + 2.41 = 3.388$; $\ln K = 3.388$; $K = e^{3.388} = 29.60$ }
14. a. 1.65kJ { $\Delta G = \Delta G^\circ + RT\ln Q$; find ΔG° from $\Delta G^\circ = -RT\ln K$; $\Delta G^\circ = -(8.314)(298.15)(\ln[7.4 \times 10^{-4}]) = 1.787 \times 10^4\text{J}$;
now find Q: $Q = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$; $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.50} = 3.16 \times 10^{-3}$; $Q = \frac{[3.16 \times 10^{-3}][0.250]}{[0.550]} = 1.44 \times 10^{-3}$;
now find ΔG : $\Delta G = \Delta G^\circ + RT\ln Q$; $\Delta G = 1.787 \times 10^4\text{J} + (8.314)(298.15)(\ln[1.44 \times 10^{-3}])$; $\Delta G = 1.787 \times 10^4\text{J} - 1.622 \times 10^4\text{J}$;
 $\Delta G = 1,651\text{J} = 1.65\text{kJ}$ }
- b. spontaneous towards the reactants since $\Delta G > 0$
15. -79.6kJ { $\Delta G = \Delta G^\circ + RT\ln Q$; use: $\Delta G^\circ_{\text{sys}} = \Sigma(n_p)\Delta_f G^\circ_{\text{products}} - \Sigma(n_r)\Delta_f G^\circ_{\text{reactants}}$ to find ΔG° ;
 $\Delta_r G^\circ = [2(\Delta_f G^\circ_{\text{NO}_2})] - [2(\Delta_f G^\circ_{\text{NO}}) + 1(\Delta_f G^\circ_{\text{O}_2})]$; $\Delta_r G^\circ = [2(51.31)] - [2(86.55) + 1(0)]$; $\Delta_r G^\circ = -70.48\text{kJ/mol}$;
 $Q = \frac{(P_{\text{NO}_2})^2}{(P_{\text{NO}})^2(P_{\text{O}_2})}$; $\Delta G = -(70.48\text{kJ})(1000\text{J/kJ}) + (8.314)(298.15)\ln\left(\frac{(0.039)^2}{(2.00)^2(0.015)}\right)$; $\Delta G = -70,480 + (2479)\ln(0.02535)$;
 $\Delta G = -79590 = -79.6\text{kJ}$ }
16. a. -5.8kJ { $\Delta G = \Delta G^\circ + RT\ln Q$; find ΔG° from $\Delta G^\circ = -RT\ln K$; $\Delta G^\circ = -(8.314)(298.15)(\ln(1.4 \times 10^{-16})) = 9.0489 \times 10^4\text{J}$;
now find Q: $Q = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$; $Q = (1.5 \times 10^{-5})^3(4.0 \times 10^{-3}) = 1.35 \times 10^{-17}$; now find ΔG : $\Delta G = \Delta G^\circ + RT\ln Q$;
 $\Delta G = 9.0489 \times 10^4\text{J} + (8.314)(298.15)(\ln[1.35 \times 10^{-17}])$; $\Delta G = 9.0489 \times 10^4\text{J} - 9.6287 \times 10^4\text{J}$; $\Delta G = -5.7979 \times 10^3\text{J} = -5.7979\text{kJ}$ }
- b. spontaneous towards the products since $\Delta G < 0$
- c. some will dissolve as this reaction will shift to the right because it is spontaneous towards the products