

Introduction

Thermodynamics and equilibrium can be a very difficult subject for the beginning chemistry student. The terminology, interpretation and application of the numerous thermodynamic variables can be daunting. Don't try to memorize each and every formula and definition. Better to try and see how they are applied to a chemical system and what information they provide for interpreting how the system will behave. Much of our analysis is how a change in temperature will affect the chemical system. Keep this in mind as you begin your journey through the thermodynamic landscape!

Definitions

The end of this document contains a summary of the important equilibrium and thermodynamic variables. Use this as a reference as we move through this worksheet. Eventually the connections between the variables will become more apparent as you work on the sample exercises.

Concept 1: $\Delta H^\circ_{\text{sys}}$ = The enthalpy change of the system.

The enthalpy change of the system, often called the "Heat of Reaction" gives the **potential energy difference** between the products and reactants under **standard conditions** (see definitions). This potential energy difference comes from several sources such as: 1) the **changes in electron potential energies** from a difference in chemical bonding between products and reactants, 2) **changes in IMF strength** during phase transitions or 3) changes in **IMF strength** (and possibly bonding) when mixing materials.

A decrease in potential energy (EXOTHERMIC) favors the forward reaction. An increase in potential energy (ENDOTHERMIC) favors the reverse reaction. The most common way to find values for $\Delta H^\circ_{\text{sys}}$ is by using tabulated values of ΔH°_f (Appendix C).

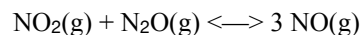
Concept 2: $\Delta S^\circ_{\text{sys}}$ = The entropy change of the system.

The entropy change of the system gives a measure of the **difference in randomness (disorder)** between the products and reactants under **standard conditions** (see definitions). An increase in randomness (disorder) as the products are formed is indicated by a positive sign for $\Delta S^\circ_{\text{sys}}$. This disorder difference comes from several sources, but is often very easy to predict using common sense.

1. For each system below, predict if the entropy of the system is increasing or decreasing.
 - 1.1. Ice melts at 0°C.
 - 1.2. A gas condenses to a liquid at 56°C.
 - 1.3. A gas is compressed into a smaller volume.
 - 1.4. A salt dissolves in water to form a solution.
 - 1.5. $\text{CaCO}_3(\text{s})$ is heated to produce $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$

An increase in the system entropy favors the forward reaction. A decrease in the system entropy favors the reverse reaction. The most common way to find values for $\Delta S^\circ_{\text{sys}}$ is by using tabulated values of S° (Appendix C).

2. Use appendix C values and Hess' Law to find $\Delta H^\circ_{\text{sys}}$ and $\Delta S^\circ_{\text{sys}}$ for the reaction below.



- 2.1. Is the reaction endo or exothermic? Is this favorable or unfavorable for the forward reaction?
- 2.2. Does the system "disorder" increase or decrease? Is this favorable or unfavorable for the forward reaction?

Concept 3: ΔS_{surr} = The entropy change of the surroundings.

The entropy change of the system is only half the story. Because most reactions do not have a nonzero enthalpy change, the surroundings will either experience a net inflow or outflow of heat. This heat flow changes the entropy of the surroundings. If heat is absorbed by the surroundings (EXOTHERMIC SYSTEM) the disorder of the surroundings increases and therefore the entropy of the surroundings will increase as well. If heat is released by the surroundings (ENDOTHERMIC SYSTEM) the disorder of the surroundings decreases and therefore the entropy of the surroundings will decrease as well. How do we quantify the change in entropy of the surroundings? It comes from $\Delta H^\circ_{\text{sys}}$ and the temperature at which the heat is transferred.

$$\Delta S_{\text{surr}} = \frac{-\Delta H^\circ_{\text{sys}}}{T}$$

3. Find ΔS_{surr} for the above reaction at 25°C. Do the surroundings become more or less ordered?

Concept 4: ΔS_{univ} = The entropy change of the universe.

Once the entropy of the system and surroundings are known we can add them together to get the entropy change of the universe. This is the basis for the **Second Law of Thermodynamics: For a spontaneous process, the entropy change of the UNIVERSE will be POSITIVE.** In another words, in a reversible process, the direction of reaction that increases the entropy of the universe ($\Delta S_{\text{univ}} > 0$) is the direction that will occur spontaneously to bring the system to equilibrium. At equilibrium, $\Delta S_{\text{univ}} = 0$.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

4. Find ΔS_{univ} for the reaction above under standard conditions at 25°C. Is the forward or reverse reaction spontaneous at 25°C?
- 4.1. Based on your calculations, is the entropy change of the system or the entropy change of the surroundings more important at 25°C in determining the direction of reaction under standard conditions?

Concept 5: $\Delta G^\circ =$ The “free energy” change under standard conditions.

Willard Gibbs was the first to define and quantify the “free energy” of a chemical system. **The “free energy” is the maximum energy available for the system to do work on the surroundings.** A spontaneous process changes from an initial state to a final state only because the final state is a lower free energy state than the initial state. The system loses free energy as it proceeds towards the final state. If this free energy can be captured then useful work can be done by the system on the surroundings. The free energy difference in the system (under standard conditions) is defined as follows:

$$\Delta G^\circ = -T\Delta S^\circ_{\text{univ}}$$

Available free energy for the forward reaction comes from the positive change in entropy of the universe at the temperature of reaction, T. Notice ΔG° and $\Delta S^\circ_{\text{univ}}$ have opposite signs. For a spontaneous reaction under standard conditions the sign of ΔG° is (–), indicating free energy decreases for the spontaneous direction of reaction and work can be done by the system. Therefore the reverse reaction is nonspontaneous. **Work must be done ON THE SYSTEM to have the nonspontaneous reverse reaction occur.**

5. Find ΔG° for the reaction above. Is the sign consistent with the spontaneous direction of reaction?

A more useful form of ΔG° can be derived (see the textbook) and is often called the **Thermodynamic Master Equation**:

$$\Delta G^\circ = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$$

6. Using this master equation, confirm you obtain the same value for ΔG° .

Concept 6: The temperature dependence of ΔG° .

KEEP IN MIND WHEN WE DISCUSS ΔH° , ΔS° , and ΔG° WE ARE COMPARING THE INITIAL (REACTANT) AND FINAL (PRODUCT) STATES UNDER STANDARD CONDITIONS, $Q = 1$. However, temperature may vary from 25°C.

The usefulness of the Master Equation cannot be overstated. This is the equation of choice for chemists who are trying to understand the temperature dependence of a chemical system. As a reminder, when the temperature of a chemical system is changed several system parameters are affected:

- The kinetics.
- The value of the equilibrium constant.
- The free energy of the system.

- Possibly the direction of spontaneous reaction.

The kinetics changes, previously studied, do not influence the thermodynamics of the system. From Le Chatelier's Principle the equilibrium constant will change depending upon the sign of $\Delta H^\circ_{\text{sys}}$. In fact as the equilibrium constant changes with temperature the spontaneous direction of reaction may also change.

Examination of the Master Equation indicates the temperature dependence of ΔG° is linear. The Master Equation can be written in the slope-intercept form.

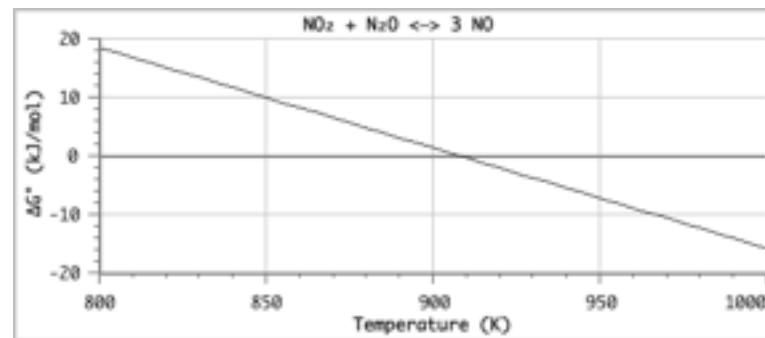
$$\Delta G^\circ = (-\Delta S^\circ_{\text{sys}})T + \Delta H^\circ_{\text{sys}}; \text{ where } (-\Delta S^\circ_{\text{sys}}) \text{ is the slope and } \Delta H^\circ_{\text{sys}} \text{ is the y-intercept.}$$

We are assuming $\Delta S^\circ_{\text{sys}}$ and $\Delta H^\circ_{\text{sys}}$ do not change appreciably with temperature. A reasonable assumption for most systems. Using $\Delta H^\circ_{\text{sys}}$ and $\Delta S^\circ_{\text{sys}}$ from above we obtain the graph shown.

A few things to notice about the temperature dependence of this system:

- The standard free energy becomes more (–) as T increases. This is because the sign of $\Delta S^\circ_{\text{sys}}$ is (+). **For systems with a (+) entropy change, increasing the temperature will always decrease ΔG° .**
- As the temperature increases the sign of ΔG° changes from (+) to (–), about 910 K on the graph. The temperature **where ΔG° passes through a value of zero is called the “cross-over” temperature, T_c , for the system.**
- For this system ΔG° is (+) below T_c indicating the reverse reaction is spontaneous below T_c . Above T_c the sign of ΔG° is (–) indicating the forward reaction is now spontaneous. This is the great influence of temperature on chemical systems, the direction of a chemical reaction can often be reversed by changing the systems temperature.

Remember, we are starting our system with $Q=1$ at every temperature.



7. Using your results from above, solve for T_c using the following equation, you should get about 910 K. (How was this equation derived?)

$$T_c = \frac{\Delta H^\circ_{\text{sys}}}{\Delta S^\circ_{\text{sys}}} =$$

In this system both $\Delta H^\circ_{\text{sys}}$ and $\Delta S^\circ_{\text{sys}}$ have the same sign, both are (+). Some systems are defined by values of $\Delta H^\circ_{\text{sys}}$ and $\Delta S^\circ_{\text{sys}}$ that have opposite signs. These systems do not have a cross-over temperature.

8. Sketch a line on the previous graph for a system where $\Delta H^\circ_{\text{sys}}$ and $\Delta S^\circ_{\text{sys}}$ are both (–).

Concept 7: ΔG° and the equilibrium constant, K_{eq} . (Constant initial state, $Q = 1$. T varies)

One of the most useful aspect of thermodynamics is the ability to predict the value of the thermodynamic equilibrium constant for a system as a function of temperature. This frees the chemist from having to measure the equilibrium constant experimentally and also gives insight into how to manipulate the system to maximize the product yield at equilibrium. Not derived in your text, the mathematical relationship between the standard free energy and the thermodynamic equilibrium constant is:

$$\Delta G^\circ = -(RT)\ln(K_{\text{eq}})$$

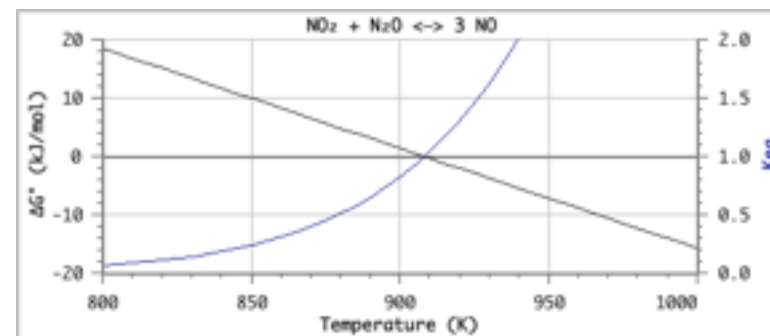
This can be rearranged to solve for K_{eq} as a function of T.

$$K_{eq} = e^{\frac{-\Delta G^\circ}{RT}} \text{ or } K_{eq} = e^{\frac{-\Delta H^\circ_{sys} + \Delta S^\circ_{sys}}{RT}} \text{ or } \ln(K_{eq}) = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ_{sys}}{RT} + \frac{\Delta S^\circ_{sys}}{R}$$

The previous graph of ΔG° is now shown with the **temperature dependence of K_{eq} plotted on the right side axis.**

A few things to notice about this system:

- K_{eq} increases as T increases. This is because the sign of ΔH°_{sys} is (+), an endothermic system. For systems with a (+) enthalpy change, increasing the temperature will always increase K_{eq} . (Le Chatelier's Principle)
- At the cross over temperature K_{eq} **passes through a value of 1.**
- Below T_c when ΔG° is (+) K_{eq} is less than 1. The reverse reaction is spontaneous under standard conditions since $Q = 1 > K_{eq}$.
- Above T_c when ΔG° is (-) K_{eq} is greater than 1. The forward reaction is spontaneous under standard conditions since $Q = 1 < K_{eq}$.



Concept 8: ΔG and Q . (Constant T, Q varies)

So far we have only considered systems that are under standard state conditions, $Q = 1$. Since this is rarely the case in the real world we need to make adjustments to the free energy based on the system being at some nonstandard state of Q , i.e., $Q \neq 1$. This is accomplished by adding a correction term to the standard free energy. We now have ΔG , the free energy as defined for any state Q at temperature T .

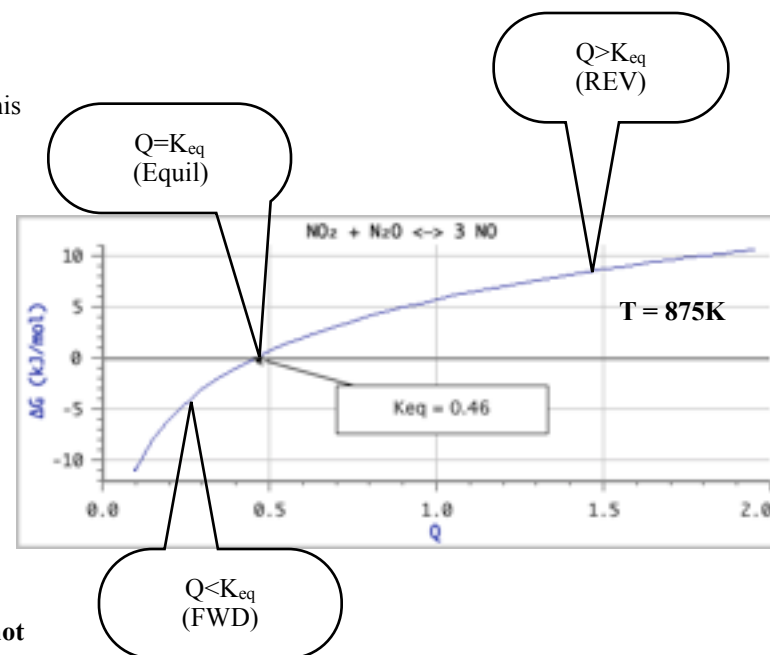
$$\Delta G = \Delta G^\circ + (RT)\ln(Q) \text{ or } \Delta G = (RT)\ln(Q/K_{eq})$$

How does this equation behave for constant temperature? Look at the graph given for the system we have studied. **The temperature is set at 875 K.** Remember when the temperature is held constant, K_{eq} is also constant and for this system has a value of 0.46 at 875 K.

A few things to notice about the system:

- ΔG increases as Q increases since we are adding a logarithmic correction term to ΔG° .
- When $Q < K_{eq}$ ΔG is (-) and the forward reaction is spontaneous.
- ΔG becomes zero when $Q = K$.
- **This is the thermodynamic definition of equilibrium, $\Delta G = 0$.**
- When $Q > K_{eq}$ ΔG is (+) and the reverse reaction is spontaneous.

Remember this graph is for constant T, therefore K_{eq} and ΔG° have fixed values and are not changing.



Review of Equilibrium and Thermodynamic Variables

Each of the thermodynamic variables (except S°) represents a change: $\Delta = (\text{product state} - \text{reactant state})$. This is the difference in state between reactants and products **under the conditions specified by T and Q.**

Variable	Meaning	How Determined	Sign	Dependence on T	Notes
$K_{\text{eq}}(T)$	Thermodynamic equilibrium constant.	Experiment or $\ln(K_{\text{eq}}) = -\Delta G^\circ/RT$ $\ln(K_{\text{eq}}) = -\Delta H^\circ_{\text{sys}}/RT + \Delta S^\circ/R$	Always (+)	T dependence through the sign of $\Delta H^\circ_{\text{sys}}$.	Final state of the system at equilibrium. $Q = K$ and $\Delta G = 0$
Q	Reaction quotient. Describes the current state of the system. Under standard conditions Q = 1.	Set by the initial conditions. Changes uniformly towards K over time.	Always (+)	No T dependence.	Q always transforms into K as the reaction proceeds. $Q < K$: fwd rxn, $\Delta G < 0$ $Q > K$: rev rxn, $\Delta G > 0$ $Q = K$: equilibrium
$^\circ$	Standard State Conditions 1 M for all (aq) reactants/products. 1 atm for all (g) reactants/products.	Pure for all (s), (l) reactants/products. $T = 298.15 \text{ K (} 25^\circ\text{C)}$ UNLESS OTHERWISE STATED.	NA	T can vary but concentrations/pressures must remain at 1	All values in Appendix C are listed for standard conditions.
$\Delta H^\circ_{\text{sys}}$ or $\Delta H^\circ_{\text{rxn}}$	The difference in potential energy between the reactants and products.	1. Appendix C using ΔH°_f 2. Calorimetric experiments 3. K_{eq} vs. T graph	(-) Exothermic Favorable for forward reaction. Potential energy decrease. Surroundings absorb heat. (+) Endothermic Unfavorable for forward reaction. Potential energy increase. Surroundings lose heat.	Very little. We will assume $\Delta H^\circ_{\text{sys}}$ remains constant.	Determines how K_{eq} changes with T. Determines $\Delta S^\circ_{\text{surr}}$ Often hard to predict the sign. $q_{\text{surr}} = -\Delta H^\circ_{\text{sys}}$
ΔH°_f	Standard heat of formation. The change in potential energy when a compound is formed from its elements under standard conditions.	Tabulated in Appendix C	(-) Exothermic Compounds are lower in potential energy than the elements. (+) Endothermic Compounds are higher in potential energy than the elements..	Very little. We will assume ΔH°_f remains constant.	Used to find $\Delta H^\circ_{\text{sys}} = \Delta H^\circ_{\text{rxn}}$ from Hess' Law

Variable	Meaning	How Determined	Sign	Dependence on T	Notes
$\Delta S^\circ_{\text{sys}}$	The difference in entropy (disorder) between the products and reactants.	1. Appendix C using S° 2. K_{eq} vs. T graph 3. ΔG° with ΔH°	(+) Favorable for the forward reaction. Products more disordered. (-) Unfavorable for the forward reaction. Products more ordered.	Very little. We will assume $\Delta S^\circ_{\text{sys}}$ remains constant.	Easy to predict the sign. Determines how ΔG° changes with T.
S° (T)	Standard molar entropy. A measure of the internal entropy of an element/compound/ion under standard conditions.	Tabulated in Appendix C	Most are (+) values except for a few aqueous ions.	Always increases with increasing T.	Used to find $\Delta S^\circ_{\text{sys}}$ from Hess' Law
$\Delta S^\circ_{\text{surr}}$ (T)	Change in entropy of the surroundings as a result of heat flow from ΔH_{sys} .	$\Delta S^\circ_{\text{surr}} = -\Delta H^\circ_{\text{sys}}/T$	(+) Favorable for the forward reaction. Surroundings more disordered. (-) Unfavorable for the forward reaction. Surroundings more ordered.	Smaller in magnitude as T increases.	Used with $\Delta S^\circ_{\text{sys}}$ to find ΔS_{univ}
$\Delta S^\circ_{\text{univ}}$ (T)	Change in entropy of the universe.	$\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}}$	(+) Forward reaction is spontaneous (-) Reverse reaction is spontaneous 0: Equilibrium State	Temperature dependence through $\Delta S^\circ_{\text{surr}}$	Second law of thermodynamics. The entropy of the universe will always increase for a spontaneous process.
ΔG° (T)	Standard "free" energy difference between products and reactants. Q = 1.	1. Appendix C using ΔG°_f (25°C) At all temperatures: 2. $\Delta G^\circ = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$ 3. $\Delta G^\circ = -RT\ln(K_{\text{eq}})$ 4. $\Delta G^\circ = -T\Delta S^\circ_{\text{univ}}$	(-) Favorable forward reaction. $K_{\text{eq}} > 1$ (+) Favorable reverse reaction. $K_{\text{eq}} < 1$ 0: $K = Q = 1$. $Q = 1$ happens to be an equilibrium state at that particular T.	Strong T dependence! Comes through the sign of ΔS_{sys} .	Thermodynamic "Master" equation $\Delta G^\circ = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$
ΔG°_f (T)	Standard "free" energy of formation. The change in "free" energy when a compound is formed from its elements under standard conditions.	Tabulated in Appendix C but only at 25°C.	(-) Favorable for compound formation. (+) Unfavorable for compound formation. Most compounds have a (-) "free" energy of formation indicating they are more stable compared to their elements at 25°C.	Strong T dependence! Comes through the sign of ΔS°_f .	Used to find ΔG° from Hess' Law ONLY at 25°C. Tabulated values at other temperatures could be estimated from $\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$

Variable	Meaning	How Determined	Sign	Dependence on T	Notes
$\Delta G(T, Q)$	The "Free" energy difference for any state defined by Q, K and T.	$\Delta G = \Delta G^\circ + RT \ln(Q)$ $\Delta G = RT \ln(Q/K_{eq})$	(-) Spontaneous forward reaction. $Q < K_{eq}$ (+) Spontaneous reverse reaction. $Q > K_{eq}$ 0: $K = Q$. Equilibrium!	Strong T dependence! Comes through the sign of ΔS_{sys} . Also depends on how K_{eq} changes with T. Complex behavior!	ΔG always approaches zero as the reaction moves towards equilibrium. Side Note: Calculating ΔG when the K_{eq}/Q ratio is very small or very large only gives an estimate of ΔG . Thermodynamics works best when we are at standard conditions or when we are not far from equilibrium.
T_c	Crossover temperature. $K_{eq} = 1, \Delta G^\circ = 0$.	$T_c = \Delta H^\circ_{sys} / \Delta S^\circ_{sys}$ Note: ΔH° and ΔS° must have the same sign for a cross over temperature to be defined.	Always (+)	None	Used to estimate the temperature of phase transitions (melting, boiling) ($K_{eq} = 1$) or when K_{eq} crosses through the value of 1 for a general equilibrium system.

General Steps for System Analysis using Thermodynamics

1. Use Appendix C values to find $\Delta H^\circ_{\text{sys}}$ and $\Delta S^\circ_{\text{sys}}$. These are CONSTANTS for your system.

1.1. Does the sign of ΔS_{sys} make common sense?

1.2. Sketch the linear graph of ΔG° versus T for this system.

1.2.1. Calculate T_c (if possible): $T_c = \frac{\Delta H^\circ_{\text{sys}}}{\Delta S^\circ_{\text{sys}}}$ T_c is now a constant for your system. At T_c what is the value of ΔG° ? What is the value of K_{eq} ?

1.3. Is this system endo- or exothermic? Will K_{eq} increase or decrease with increasing T?

1.3.1. Sketch the nonlinear graph of K_{eq} versus T for this system.

2. Set your temperature, T. Calculations are now done at this T assuming STANDARD CONDITIONS, Q = 1. (If no temperature is given assume 298.15 K.)

2.1. Find ΔG° : $\Delta G^\circ = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$. Draw a conclusion: Is the reverse or forward reaction favored under standard conditions?

2.2. Find K_{eq} : $K_{\text{eq}} = e^{-\Delta G^\circ/RT}$ Does the value of K_{eq} agree with your conclusion in 2.1? Remember, Q = 1. Compare K_{eq} to 1.

2.3. Find $\Delta S^\circ_{\text{surr}} = \frac{-\Delta H^\circ_{\text{sys}}}{T}$

2.4. Find $\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}}$ Does the sign of $\Delta S^\circ_{\text{univ}}$ agree with your conclusion in 2.1?

2.5. If required, use an ICE table to take the system from Q = 1 to the equilibrium state defined by K_{eq} .

2.6. If non-standard conditions are specified then determine the value of Q.

2.6.1. Find $\Delta G = \Delta G^\circ + RT\ln(Q)$ or $\Delta G = RT\ln(Q/K_{\text{eq}})$ Draw a conclusion: does the sign of ΔG agree with your values of Q and K_{eq} ?

2.6.2. Find $\Delta S_{\text{univ}} = \frac{\Delta G}{-T}$

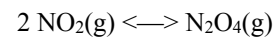
2.6.3. If required, use an ICE table to take the system from Q to the equilibrium state defined by K_{eq} .

2.7. If you change Q, go back to step 2.6

3. If you change T, go back to step 2 for the new T.

Thermodynamics WorkSheet for Chemistry 1B

You now have the tools to completely analyze a simple system thermodynamically. For the following system complete the indicated analysis.



1. Find $\Delta H^\circ_{\text{sys}}$ and $\Delta S^\circ_{\text{sys}}$ using Appendix C.

2. Calculate $\Delta S^\circ_{\text{surr}}$ and $\Delta S^\circ_{\text{univ}}$ at 25°C

2.1. Is the forward or reverse reaction spontaneous at 25°C?

3. Calculate $\Delta S^\circ_{\text{surr}}$ and $\Delta S^\circ_{\text{univ}}$ at 100°C

3.1. Is the forward or reverse reaction spontaneous at 100°C?

4. Calculate ΔG° and K_{eq} at 25°C .

4.1. Compare K_{eq} to $Q = 1$. Is the sign of ΔG° consistent with this comparison?

5. Sketch a graph of ΔG° versus T for his system. Find T_c . Under standard conditions over what temperature range is the forward reaction spontaneous?

6. Sketch a graph of K_{eq} versus T for this system. At what temperature does K_{eq} pass through the value of 1?

7. Find the temperatures where the equilibrium constant has a value of 0.01 and 100 respectively.
8. **Nonstandard conditions.** If the partial pressure of each gas is set a 5.0 atm at 25°C, is the system at equilibrium? Hint: find Q!
- 8.1. In which direction will the system react to achieve equilibrium?
- 8.2. Calculate the value of ΔG for this system.
9. An experimenter begins with the system at standard conditions at 25°C. When equilibrium is achieved, what will be the partial pressures of each gas? (Might need your TI calculator for this one!)

- 9.1. The experimenter wants to change the equilibrium mixture of gases she has at 25°C to an equilibrium mixture where there is 10 times as much N₂O₄ as NO₂. What is the partial pressure of each gas when a system gas ratio of 10/1 is achieved? To what temperature should she take the system to achieve this 10/1 ratio?

Hints: Solve an *ICF* table using your 25 °C pressures (previous problem) as the initial partial pressures. Set your final state, *F*, to a 10/1 ratio, not an

equilibrium value of 10. Solve for the ratio of pressures, $\frac{P_{N_2O_4}}{P_{NO_2}} = 10$ (no square on the NO₂). Once you have these two pressures use them to

calculate K_{eq} (now you square the NO₂ pressure!). Use this K_{eq} to find a T as you did in previous calculations. Good Luck!