

Thermodynamic Calculations

- Before we get further into changes in enthalpy, ΔH 's, changes in entropy, ΔS 's, and subsequently changes in Gibbs free energy, ΔG 's, there is a notational mess that should be clarified. The value of thermodynamic quantities H , S , G , etc., depend upon the conditions under which they are measured. The standard notation used to identify the conditions are as follows:

ΔH°_{298} , ΔS°_{298} , ΔG°_{298}	– Taken for a pure substance at 1 atm and 298 K.
ΔH° , ΔS° , ΔG°	– Taken for a pure substance
ΔH , ΔS , ΔG	– No restrictions

This issue of the conditions or state at which the problem is occurring doesn't come into play very much for AP chemistry. The tables you work with are all for pure substances at 1 atm and 298 K. It will come into play a little bit with Gibbs free energy, and you should just be aware that when the symbols slightly change, it's intentional and that's why temperature and pressure are always given in problem statements.

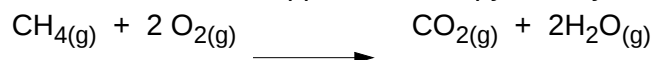
Things you are already supposed to know

- Remember how to calculate ΔH°_{298} from heats of formation data --> you'll use it again.

Things you are supposed to learn now

- Calculating ΔS°_{298} 's are very similar to calculating ΔH°_{298} 's. It's the same products minus reactants deal you having to account for the reaction's stoichiometry. The only big difference, and this is really important, is that **elemental species have S°_{298} values**.

For example: Let's take a look at what happens to entropy when you burn some decayed dinosaur dookie.



$$\Delta S^\circ_{298} = (\sum v_i S^\circ_{i^\circ})_{\text{products}} - (\sum v_i S^\circ_{i^\circ})_{\text{reactants}}$$

Look all the S°_{298} values up on a table

$$\Delta S^\circ_{298} = [(1)(213.6 \text{ J/mol}\cdot\text{K}) + (2)(188.7 \text{ J/mol}\cdot\text{K})] - [(1)(219.5 \text{ J/mol}\cdot\text{K}) + (2)(205 \text{ J/mol}\cdot\text{K})]$$

$$\begin{array}{ccccccc} \uparrow & & \uparrow & & \uparrow & & \uparrow \\ S^\circ_{298} \text{ for CO}_2(\text{g}) & & S^\circ_{298} \text{ for H}_2\text{O}(\text{g}) & & S^\circ_{298} \text{ for CH}_4(\text{g}) & & S^\circ_{298} \text{ for O}_2(\text{g}) \\ \Delta S^\circ_{298} = -38.5 \text{ J/mol}\cdot\text{K} & & & & & & \text{(elements have values!)} \end{array}$$

Now, you might be saying to yourself "this is a decrease in entropy and I know that methane combusts so isn't that inconsistent with the whole second law thing?" The answer is no. For the second law you have to look at the entropy change of the universe, and what we just calculated would be the entropy change of the system. So let's get the entropy change of the surroundings and add them together.

$$\begin{aligned} \Delta S_{\text{universe}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -38.5 \text{ J/mol}\cdot\text{K} + \Delta S_{\text{surroundings}} \\ \Delta S_{\text{surroundings}} &= \frac{q_{\text{surr}}}{T} = \frac{-\Delta H_{\text{rxn}}}{T} = \frac{-(-802,300 \text{ J/mol})}{298 \text{ K}} = 2,692 \text{ J/mol}\cdot\text{K} \end{aligned}$$

Soooooo, the entropy change of the universe = $2,654 \text{ J/mol}\cdot\text{K} > 0$ which means spontaneous craziness.

- Gibbs (J. Willard) put this whole spontaneity thing together and named it after himself or somebody else named it after him or something. Anyway, we got the Gibbs-Helmholtz equation:

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

ENERGY vs. ENTROPY

← the balance of nature

The sign of ΔG from the G-H equation tells us about spontaneity:

- $\Delta G = 0$ The system is at equilibrium
 $\Delta G < 0$ Spontaneous
 $\Delta G > 0$ Not spontaneous

You can predict general trends in reaction spontaneity .
 Remember T is absolute temp, it never has a negative sign.

<u>ΔH</u>	<u>ΔS</u>	<u>ΔG</u>
+	+	High T, is spontaneous in the forward direction Low T, is spontaneous in the reverse direction
+	-	Always > 0 , reverse rxn is spontaneous
-	+	Always < 0 , forward rxn is spontaneous
-	-	Low T, the forward rxn is spontaneous High T, the reverse rxn is spontaneous

You can calculate ΔG° from ΔH° , ΔS° , and T values or you can look up standard free energies of formation, ΔG°_f , and use the products minus reactants procedure. Elemental species don't have values for standard free energies of formation, ΔG°_f .

Basically this represents 4 unknowns in an equation, anyone of which you can solve for given the other 3.

There are also nonstandard values of ΔG

- A. To get ΔG at a different temperature and concentrations from the standard state value

$$\Delta G = \Delta G^\circ + RT \ln Q_c \quad \text{where } Q_c = \text{reaction quotient}$$

- B. You can also get ΔG° from or use ΔG° to get an equilibrium constant for a reaction. At equilibrium $\Delta G = 0$ so it falls out of the previous equation and you get the following:

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

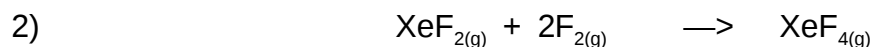
This links T, ΔH , ΔS to K_{sp} i.e. **thermodynamics determines equilibrium.**

Student Packet: 7.5: Thermodynamic Calculations: AssessMe questions

- 1) A "state function" is a mathematical function which
- A) is dependent on the exact path which is followed by a process.
 - B) only depends on the initial conditions and the final conditions of the process.
 - C) specifically describes changes in the energy content of a molecular system.
 - D) presents the integral of a quantity with respect to time.
 - E) I'm clueless
- 2) Which of the following is a state function:
- A) The change in potential energy as a ball is dropped from a 10 story building.
 - B) The length of time needed for a ball to travel down a mountainside.
 - C) The final velocity of a ball dropped out a window.
 - D) The distance a ball will travel if kicked from the top of a hill in such manner that the ball never loses contact with the ground.
 - E) I'm clueless
- 3) Which of the following statements is true?
- A) A spontaneous reaction must occur.
 - B) All spontaneous reactions occur rapidly.
 - C) A non-spontaneous reaction cannot occur.
 - D) Spontaneous is a term related to the kinetics of a reaction.
 - E) I'm clueless
- 4) The forward direction of a reaction will be spontaneous if the following mathematical relationship is true (where Q is the reaction quotient and K is the equilibrium constant).
- A) $Q=K$ B) $Q<K$ C) $Q>K$ D) $Q=K^2$ E) I'm clueless
- 5) What is the value of $-\log[\text{OH}^-]$ for a pH=4 solution?
- A) 4 B) 7 C) 10 D) 12 E) I'm clueless
- 6) Consider the autoionization of liquid ammonia:
- $$2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^- \text{ with } pK_{\text{NH}_3} = 27$$
- What is the concentration of $[\text{NH}_4^+]$ in a neutral solution of liquid ammonia?
- A) 13.5M B) $3.2 \times 10^{-14}\text{M}$ C) $1.0 \times 10^{-27}\text{M}$ D) $1.0 \times 10^{-7}\text{M}$ E) I'm clueless

Student Packet: 7.5: Thermodynamic Calculations: ShowMe questions

- 1) When the pressure on a 33.9 g sample of monatomic ideal gas at 298 K is increased from 1 atm to 300 atm, the Gibbs free energy increased by 12 kJ. What is the gas?



Calculate K for this reaction at 298 K, given the following DG_f° information.

$$\text{DG}_f^\circ \text{XeF}_{2(g)} = -48 \text{ kJ/mol}, \quad \text{DG}_f^\circ \text{XeF}_{4(g)} = -121 \text{ kJ/mol}$$

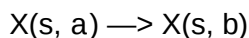
- 3) The equilibrium constant for a certain reaction increases by a factor of 20 when the temperature is increased from 300 K to 500 K. Calculate the standard change in enthalpy for this reaction, assuming it is temperature-dependent.

- 4) 1.00 mole of neon gas is heated from 25.0°C to 150°C at constant volume. Calculate g, w, DU, and DH for this process.

$$(C_v \text{ of Ne} = 12.47 \text{ J/Kmol}, \quad C_p \text{ of Ne} = 20.80 \text{ J/Kmol})$$

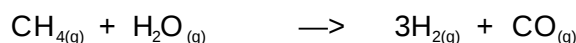
Student Packet: 7.5: Thermodynamic Calculations: TestMe questions

- 1) A certain material exists in two crystalline forms, a and b. The a form is initially obtained when the liquid freezes. However, below 173 K the a form spontaneously converts to the b form.



Predict the signs of ΔH and ΔS for this process.

- A) $\Delta H > 0$, $\Delta S > 0$
 B) $\Delta H > 0$, $\Delta S < 0$
 C) $\Delta H < 0$, $\Delta S < 0$
 D) $\Delta H < 0$, $\Delta S > 0$
 E) Cannot be determined from the information given.
- 2) Calculate the standard change in Gibbs free energy of the following reaction when it is carried out at 25°C and 1 atm external pressure, based on the provided data.



Substance	ΔH_f° (kJ/mol)	S° (J/Kmol)
$\text{CH}_4(g)$	-75	186
$\text{H}_2\text{O}(g)$	-242	189
$\text{CO}(g)$	-110.5	198
$\text{H}_2(g)$	0	131

- A) 271 kJ/mol B) 201 kJ/mol C) -64.2 kJ/mol D) 142 kJ/mol E) -5.19 kJ/mol
- 3) Two moles of an ideal gas are contained in a cylinder with a movable piston. The temperature is constant at 25°C. Weights are removed suddenly from the top of the cylinder (so that the gas expands irreversibly) to give the following series of pressures:
 $P_1 = 3.00$ atm (initial state)
 $P_2 = 1.00$ atm
 $P_3 = 0.75$ atm (final state)
 What is the total work done by the gas in this process?
- A) -4.54 kJ B) -13.2 kJ C) -0.381 kJ D) -3.72 kJ E) -6.87 kJ
- 4) Calculate the equilibrium constant of the following reaction of 298 K, based on the information provided.



	ΔH_f° (kJ/mol)	S° (J/Kmol)
$\text{NO}(g)$	90	211
$\text{NO}_2(g)$	34	240
$\text{O}_2(g)$	0	205

- A) 4.3×10^{-19} B) 1.03 C) 9.0×10^{-11} D) 1.1×10^4 E) -68.2
- 5) What is the change in Gibbs free energy (ΔG) for the autoionization of water at 25°C when $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-9} \text{ M}$?
- A) 1.0×10^{-14} B) 80.0 kJ/mol C) -23 kJ/mol D) -1.9 kJ/mol E) 6.4 kJ/mol