

Thermodynamics1Key

Monday, November 07, 2016 7:29 AM

Thermodynamics

1. Consider the following reaction at equilibrium.

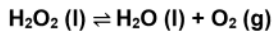


- Is heat a product or a reactant for this reaction? How do you know?
At <math>\Delta H < 0</math>, exothermic. Heat is produced
- What will the sign of ΔG° be? $\Delta G^{\circ} > 0$ $\Delta G^{\circ} < 0$
when $K > 1$, $\Delta G^{\circ} < 0$ (products favored)
- Under standard conditions, is this reaction spontaneous?
Yes. $\Delta G^{\circ} < 0$
- What is the sign of ΔS° ? $\Delta S^{\circ} > 0$ $\Delta S^{\circ} < 0$ Cannot determine
 $\Delta G = \Delta H - T\Delta S$. $\Delta G < 0$ and $\Delta H < 0$ are both (-). ΔS could be (+) or (-)
- For each of the following, determine if the equilibrium will shift toward products or reactants or if there will be no change.
 - The temperature is increased in a flask that was at equilibrium. React \Rightarrow prod Heat
 - ZnO (s) is added to the reaction chamber. no change
 - Carbon monoxide is added to the chamber. React. CO is a product

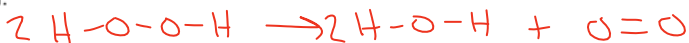
2. For each change listed in Problem 1e, determine if:

- | | | | |
|----------------------------------|-----------------------------|-------------------------------|-------------------------------|
| a. $Q < K$, | $Q > K$, | $Q = K$ | i. $Q > K$, $\Delta G > 0$ |
| b. $\Delta G_{\text{rxn}} > 0$, | $\Delta G_{\text{rxn}} < 0$ | $\Delta G_{\text{rxn}} = 0$. | ii. $Q = K$, $\Delta G = 0$ |
| | | | iii. $Q > K$, $\Delta G > 0$ |

For problems 3-9, refer to this reaction:



3. Use the table of bond enthalpies below to determine ΔH° . Is the reaction is enthalpically favorable (a favorable reaction contributes to a spontaneous reaction). Note that the reaction is not necessarily balanced.



$$4(464) + 2(142) + 4(-464) + -502$$

$$\Delta H = -218 \frac{\text{kJ}}{\text{mol}}$$

4. Is the equilibrium constant is larger at 100 K or 250 K? Clearly justify your answer.

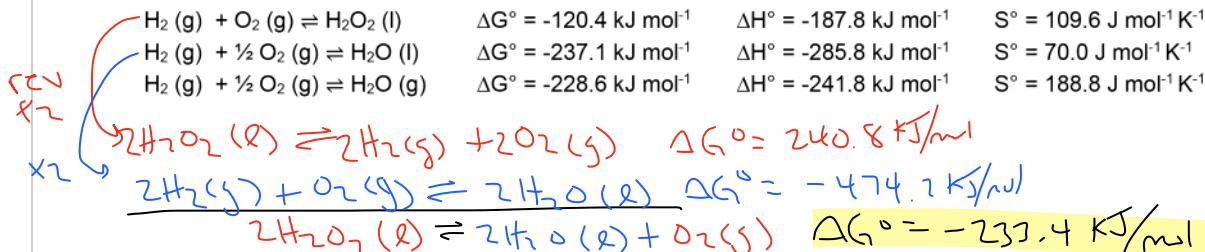
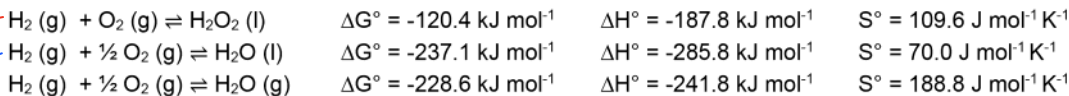
$\Delta H < 0$, so heat is a prod. Increasing T will shift the equilbr. \rightarrow make more react. $T, \downarrow K$

5. From your answer to problem 3, determine ΔH° for each of these reactions:

- $3 \text{H}_2\text{O}_2(\text{l}) \rightleftharpoons 3 \text{H}_2\text{O}(\text{l}) + 3 \text{O}_2(\text{g})$ $3(-218) = -654 \text{ kJ/mol}$
- $\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}_2(\text{l})$ *reverse* $\Delta H = 218 \text{ kJ/mol}$
- $4 \text{H}_2\text{O}(\text{l}) + 4 \text{O}_2(\text{g}) \rightleftharpoons 4 \text{H}_2\text{O}_2(\text{l})$ $\text{rev} \times 4$ $\Delta H = 4(218) = 872 \text{ kJ/mol}$

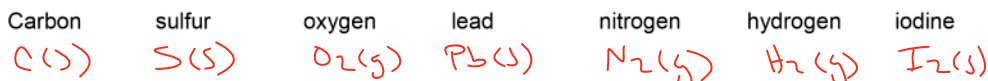
Yes, I made an error here! Ignore!

6. Use the following information to calculate ΔG° for the decomposition of H_2O_2 :



7. The values listed in problem 6 are known as formation energies – the ΔG , ΔH , and S required to create a compound from its most stable elemental components. They are incredibly useful because they have been measured and tabulated so they are very easy to find. Consequently, you are able to calculate ΔH , ΔG , and ΔS for absolutely any reaction!

a. The most stable form of most elements is an elemental solid; however, the common diatomic molecules are in their most stable form as diatomic molecules. Determine the most stable form of the following elements:



b. As you saw in problem 6, you can use these reactions in Hess' Law to calculate ΔG , ΔH , or ΔS for a reaction...but there is an easier way! Add up the formation energy of products. Add up to formation energy of reactants. Now products minus reactants. And done.

Using the information in problem 6, calculate ΔG° , ΔH° , and ΔS° . Does ΔG° match what you found in problem 6?

$$\Delta G^\circ = 2(-237.1) - (2(-120.4)) = -233.4 \text{ kJ/mol}$$

$$\Delta H^\circ = 2(-285.8) - (2(-187.8)) = -196 \text{ kJ/mol}$$

$$\Delta S^\circ = [2(70) + 205.2] - (2(109.6)) = 126 \text{ J/mol}\cdot\text{K}$$

O_2 is included in ΔS calculation because it is NOT \emptyset !

8. If 50 g of H_2O_2 is allowed to decompose, determine how much heat is released. Assume 100% yield. (Hint: ΔH° has the units of kJ/mol, so use it as a conversion factor!)

$$\frac{50 \text{ g } H_2O_2}{34.02 \text{ g}} \times \frac{-196 \text{ kJ}}{2 \text{ mol } H_2O_2} = -144 \text{ kJ of heat}$$

\rightarrow 2 mol of H_2O_2 in balanced reaction

9. Calculate K at 25 °C.

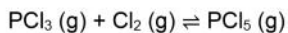
$$\Delta G^\circ = -RT \ln K$$

$$-233.4 \frac{\text{kJ}}{\text{mol}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} (298.15 \text{ K}) \ln K$$

$$\ln K = 94.16$$

$$K = 7.8 \times 10^{40}$$

10. Consider the reaction below. For the reaction below, calculate ΔG when the indicated concentrations are mixed together at 75 °C. Report your answer in kJ mol⁻¹.



$$[\text{Cl}_2] = 0.5 \text{ M} \quad [\text{PCl}_3] = 0.1 \text{ M} \quad [\text{PCl}_5] = 0.1 \text{ M}$$

$$K = 1.1 \times 10^5 \text{ at } 75^\circ\text{C}$$

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

$$\Delta G^\circ = -8.314 (273.15 + 75) \ln 1.1 \times 10^5$$

$$Q = \frac{[\text{PCl}_5]}{[\text{Cl}_2][\text{PCl}_3]}$$

$K > Q$ so
 $\Delta G < 0$

$$\Delta G^\circ = -33,600 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G = -33,600 + (8.314)(273.15 + 75) \ln 2$$

$$Q = \frac{0.1}{(0.1)(0.5)} = 2$$

$$\Delta G = -31593.7 \frac{\text{kJ}}{\text{mol}}$$

11. Consider the reaction in problem 10. The same reaction has a $K = 1.25 \times 10^2$ at 175 °C.

- Is the reaction endothermic or exothermic?
- Calculate ΔH .

$T \uparrow \Rightarrow K \downarrow$, so this means

that it is exothermic

react \Rightarrow prod + heat

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{1.25 \times 10^2}{1.1 \times 10^5} = \frac{\Delta H}{8.314} \left(\frac{1}{348.15} - \frac{1}{448.15} \right)$$

$$-6.78 = \Delta H (7.71 \times 10^{-5})$$

$$\Delta H = -87948 \text{ J/mol}$$

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

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

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

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$R = 8.314 \frac{\text{J}}{\text{mol K}}$$

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Bond	Molar bond enthalpy, $H_{\text{bond}}/\text{kJ}\cdot\text{mol}^{-1}$	Bond	Molar bond enthalpy, $H_{\text{bond}}/\text{kJ}\cdot\text{mol}^{-1}$
O-H	464	C≡N	890
O-O	142	N-H	390
C-O	351	N-N	159
O=O	502	N=N	418
C=O	730	N≡N	945
C-C	347	F-F	155
C=C	615	Cl-Cl	243
C≡C	811	Br-Br	192
C-H	414	H-H	435
C-F	439	H-F	565
C-Cl	331	H-Cl	431
C-Br	276	H-Br	368
C-N	293	H-S	364
C=N	615		

TABLE 14.5 Average molar bond enthalpies

TABLE 23.1 Standard molar entropies (S°), enthalpies of formation (ΔH_f°), and Gibbs energies of formation (ΔG_f°) of various substances at 25°C and one bar (see also Appendix D)*

Substance	$S^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta H_f^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta G_f^\circ / \text{kJ}\cdot\text{mol}^{-1}$	Substance	$S^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta H_f^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta G_f^\circ / \text{kJ}\cdot\text{mol}^{-1}$
Ag(s)	42.6	0	0	H ₂ O ₂ (l)	109.6	-187.8	-120.4
AgCl(s)	96.3	-127.0	-109.8	H ₂ S(g)	205.8	-20.6	-33.4
C(s, diamond)	2.4	1.9	2.9	N(g)	153.3	472.7	455.5
C(s, graphite)	5.7	0	0	N ₂ (g)	191.6	0	0
CH ₄ (g)	186.3	-74.6	-50.5	NH ₃ (g)	192.8	-45.9	-16.4
C ₂ H ₂ (g)	200.9	227.4	209.9	N ₂ H ₄ (l)	121.2	50.6	149.3
C ₂ H ₄ (g)	219.3	52.4	68.4	NO(g)	210.8	91.3	87.6
C ₆ H ₆ (l)	173.4	49.1	124.5	NO ₂ (g)	240.1	33.2	51.3
CH ₃ OH(l)	126.8	-239.2	-166.6	N ₂ O(g)	220.0	81.6	103.7
CH ₃ Cl(g)	234.6	-81.9	-58.4	N ₂ O ₄ (g)	304.4	11.1	99.8
CH ₃ Cl(l)	145.3	-102	-51.5	N ₂ O ₅ (s)	178.2	-43.1	113.9
CH ₂ Cl ₂ (g)	270.2	-95.4	-68.8	Na(g)	153.7	107.5	77.0
CH ₂ Cl ₂ (l)	177.8	-124.2	-70.0	Na(s)	51.3	0	0
CHCl ₃ (g)	295.7	-102.7	6.0	O(g)	161.1	249.2	231.7
CHCl ₃ (l)	201.7	-134.1	-73.7	O ₂ (g)	205.2	0	0
CO(g)	197.7	-110.5	-137.2	P(s, white)	41.1	0	0
CO ₂ (g)	213.8	-393.5	-394.4	P(s, red)	22.8	-17.6	-12.1
Cl(g)	165.2	121.3	105.3	PCl ₃ (g)	311.8	-287.0	-267.8
Cl ₂ (g)	223.1	0	0	PCl ₅ (g)	364.6	-374.9	-305.0
H(g)	114.7	218.0	203.3	S(s, rhombic)	28.5	0	0
H ₂ (g)	130.7	0	0	S(s, monoclinic)	32.6	0.3	0.1
H ₂ O(g)	188.8	-241.8	-228.6	SO ₂ (g)	248.2	-296.8	-300.1
H ₂ O(l)	70.0	-285.8	-237.1	SO ₃ (g)	256.8	-395.7	-371.1

*Most data from *CRC Handbook of Chemistry and Physics*, 87th Online Edition, 2006–2007.

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