

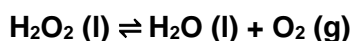
## Thermodynamics

1. Consider the following reaction at equilibrium. For each of the following, determine if the equilibrium will shift toward products or reactants or if there will be no change.

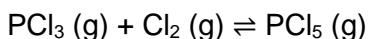


- The temperature is increased in a flask that was at equilibrium.
  - ZnO (s) is added to the reaction chamber.
  - Carbon monoxide is added to the chamber.
2. For each change listed in Problem 2, determine if  $\Delta G_{\text{rxn}} > 0$ ,  $\Delta G_{\text{rxn}} < 0$ , or  $\Delta G_{\text{rxn}} = 0$ .

For problems 3-8, refer to this reaction:



- Use the table of bond enthalpies below, (Table 14.5 in your textbook) predict if the following reaction is enthalpically favorable. Note that the reaction is not necessarily balanced.
- Is the equilibrium constant is larger at 100 K or 250 K? Clearly justify your answer.
- Without doing any math, determine if  $\Delta S_{\text{rxn}} > 0$  or  $\Delta S_{\text{rxn}} < 0$ .
- Using Appendix D in your book, calculate  $\Delta H_{\text{rxn}}^{\circ}$ ,  $\Delta S_{\text{rxn}}^{\circ}$ ,  $\Delta G_{\text{rxn}}^{\circ}$ .
- The density of  $\text{H}_2\text{O}_2$  is 1.443 g/mL. If 50 mL of  $\text{H}_2\text{O}_2$  is allowed to decompose, determine  $\Delta H$ . Assume 100% yield
- Calculate K at 25 °C.
- For the reaction below, calculate  $\Delta G_{\text{rxn}}$  when the indicated concentrations are mixed together at 75 °C. Report you answer in  $\text{kJ mol}^{-1}$ .



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

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

10. Consider the evaporation of  $\text{CH}_2\text{Cl}_2$ .
- Without doing any math, predict the sign of  $\Delta H$ . Does this contribute to or oppose spontaneity?
  - Without doing any math, predict the sign of  $\Delta S$ . Does this contribute to or oppose spontaneity?
  - Using the information in Table 23.1, determine the boiling temperature. Note that this is when the products and reactants are in equilibrium ( $Q = K$  and  $\Delta G = 0$ ).

## Thermodynamics Equations

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

$$\Delta G^0 = -RT\ln K$$

$$\Delta G = \Delta G^0 + RT\ln Q$$

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

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

**TABLE 14.5** Average molar bond enthalpies

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 23.1** Standard molar entropies ( $S^\circ$ ), enthalpies of formation ( $\Delta H_f^\circ$ ), and Gibbs energies of formation ( $\Delta G_f^\circ$ ) 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 <sub>2</sub> O <sub>2</sub> (l)	109.6	-187.8	-120.4
AgCl(s)	96.3	-127.0	-109.8	H <sub>2</sub> 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 <sub>2</sub> (g)	191.6	0	0
CH <sub>4</sub> (g)	186.3	-74.6	-50.5	NH <sub>3</sub> (g)	192.8	-45.9	-16.4
C <sub>2</sub> H <sub>2</sub> (g)	200.9	227.4	209.9	N <sub>2</sub> H <sub>4</sub> (l)	121.2	50.6	149.3
C <sub>2</sub> H <sub>4</sub> (g)	219.3	52.4	68.4	NO(g)	210.8	91.3	87.6
C <sub>6</sub> H <sub>6</sub> (l)	173.4	49.1	124.5	NO <sub>2</sub> (g)	240.1	33.2	51.3
CH <sub>3</sub> OH(l)	126.8	-239.2	-166.6	N <sub>2</sub> O(g)	220.0	81.6	103.7
CH <sub>3</sub> Cl(g)	234.6	-81.9	-58.4	N <sub>2</sub> O <sub>4</sub> (g)	304.4	11.1	99.8
CH <sub>3</sub> Cl(l)	145.3	-102	-51.5	N <sub>2</sub> O <sub>5</sub> (s)	178.2	-43.1	113.9
CH <sub>2</sub> Cl <sub>2</sub> (g)	270.2	-95.4	-68.8	Na(g)	153.7	107.5	77.0
CH <sub>2</sub> Cl <sub>2</sub> (l)	177.8	-124.2	-70.0	Na(s)	51.3	0	0
CHCl <sub>3</sub> (g)	295.7	-102.7	6.0	O(g)	161.1	249.2	231.7
CHCl <sub>3</sub> (l)	201.7	-134.1	-73.7	O <sub>2</sub> (g)	205.2	0	0
CO(g)	197.7	-110.5	-137.2	P(s, white)	41.1	0	0
CO <sub>2</sub> (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 <sub>3</sub> (g)	311.8	-287.0	-267.8
Cl <sub>2</sub> (g)	223.1	0	0	PCl <sub>5</sub> (g)	364.6	-374.9	-305.0
H(g)	114.7	218.0	203.3	S(s, rhombic)	28.5	0	0
H <sub>2</sub> (g)	130.7	0	0	S(s, monoclinic)	32.6	0.3	0.1
H <sub>2</sub> O(g)	188.8	-241.8	-228.6	SO <sub>2</sub> (g)	248.2	-296.8	-300.1
H <sub>2</sub> O(l)	70.0	-285.8	-237.1	SO <sub>3</sub> (g)	256.8	-395.7	-371.1

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

- ① a) The reaction is exothermic ( $\Delta H < 0$ ), so heat is a product. Increasing the temperature will increase [Products] - so the reaction will shift to reactants
- b)  $ZnO$  is a solid. Solids don't influence the equilibrium. No change
- c)  $CO$  is a product. Reactants will form

2.  $\Delta G = 0$  if no change  $\Delta G < 0$  if products form  $\Delta G > 0$  if reactants form

- a)  $\Delta G > 0$   
 b)  $\Delta G = 0$   
 c)  $\Delta G > 0$



Bonds to break:

$$\begin{array}{l} H-O \times 4 \rightarrow 4(464 \text{ kJ/mol}) = 1856 \text{ kJ/mol} \\ O-O \times 2 \rightarrow 2(142 \text{ kJ/mol}) = 284 \text{ kJ/mol} \end{array}$$

$$\text{Total Endothermic} = 1856 + 284 = 2140 \text{ kJ/mol}$$

Bonds to make:

$$\begin{array}{l} 4 \times O-H \rightarrow 4(-464 \text{ kJ/mol}) = -1856 \text{ kJ/mol} \\ O=O \rightarrow -502 \text{ kJ/mol} \end{array}$$

$$\text{Total exothermic} = -1856 + -502 = -2358 \text{ kJ/mol}$$

$$\Delta H = 2140 + -2358 \text{ kJ/mol} = -218 \text{ kJ/mol}$$

- ④ Since  $\Delta H$  is exothermic, heat is a product. This means that  $T$  will  $\uparrow$  the product consequently, more reactants will be made and  $K$  will decrease.

$$\boxed{100^\circ C}$$

⑤  $\Delta S > 0$ . In this reaction, we start with 2 molecules + make 3.  
 Also,  $\Delta n_{\text{gas}} = 1$ . Both of these suggest a favorable entropy.

⑥

		$2 \text{H}_2\text{O}_2 (\ell)$	$\Rightarrow$	$2 \text{H}_2\text{O} (\ell)$	$+ \text{O}_2 (\text{g})$
KJ/mol	$\Delta H_f^\circ$	-187.8		-285.8	0
KJ/mol	$\Delta G_f^\circ$	-120.4		-237.1	0
J/mol·K	$S^\circ$	109.6		70	205.2

$$\Delta H = [2(-285.8) + 0] - 2(-187.8) = -196 \text{ KJ/mol}$$

$$\Delta G = [2(-237.1) + 0] - 2(-120.4) = -233.4 \text{ KJ/mol}$$

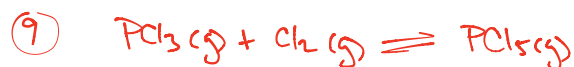
$$\Delta S = [2(70) + 205.2] - 2(109.6) = 219.2 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

⑦  $\frac{50 \text{ mL} | 1.443 \text{ g} | \frac{\text{mol}}{34.02 \text{ g}}}{\text{mL}} = 2.12 \text{ mol H}_2\text{O}_2 \frac{-196 \text{ KJ}}{2 \text{ mol H}_2\text{O}_2} = -207.84 \text{ KJ}$

⑧  $\Delta G^\circ = -RT \ln K$

$$-233.4 \frac{\text{KJ}}{\text{mol}} \frac{10^3 \text{ J}}{1 \text{ KJ}} = -233400 \frac{\text{J}}{\text{mol}} = -8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} (298.15 \text{ K}) \ln K$$

$$\ln K = 94.16 \quad K = 7.8 \times 10^{40} \quad (\text{Products are REALLY favored!})$$



$$Q = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{0.1}{(0.1)(0.5)} = 2$$

$Q < K$ , so too many reactants

- products will form

-  $\Delta G$  should be negative (spontaneous)

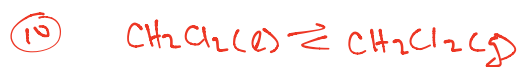
$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} (273.15 \text{ K} + 75) \ln (1.1 \times 10^5)$$

$$\Delta G = \frac{-33600 \text{ J}}{\text{mol}} + 8.314 (273.15 + 75) \ln 2$$

$$\Delta G^\circ = -33600 \frac{\text{J}}{\text{mol}}$$

$$\Delta G = -31,593.9 \frac{\text{J}}{\text{mol}}$$



a)  $l \rightarrow g$  this requires heat (think boiling water)  $\Delta H > 0$   
 $\hookrightarrow$  endothermic - opposes

b)  $\Delta n_{\text{gas}} = 1$  more gas created  $\Delta S > 0$  contributes

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

$0 = \Delta H - T\Delta S$

calculating these let us calculate  $T_b$

	$\text{CH}_2\text{Cl}_2(l)$	$\rightleftharpoons$	$\text{CH}_2\text{Cl}_2(g)$	
$\Delta H_f^\circ$	-124.2		-95.4	$\Delta H = [-95.4] - [-124.2] = 28.8 \text{ kJ/mol}$
$S^\circ$	177.8		270.2	$\Delta S = [270.2] - [177.8] = 92.4 \frac{\text{J}}{\text{mol}\cdot\text{K}}$

$$0 = 28,800 \frac{\text{J}}{\text{mol}} - T \left( 92.4 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$$

$$\left( 92.4 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) T = 28,800 \frac{\text{J}}{\text{mol}}$$

$$T = 311.7 \text{ K} = 38.54^\circ\text{C}$$