

ICE1.1a. Under what circumstances will an endothermic reaction be spontaneous?

**Endothermic reactions are spontaneous when the  $\Delta S$  is positive, and the absolute magnitude of  $-T\Delta S$  exceeds  $\Delta H$  for the reaction.**

- b) Under what circumstances of  $\Delta H$  and  $\Delta S$  will a reaction be spontaneous at one temperature and nonspontaneous at a higher temperature?

**Reactions that are spontaneous at a low temperature and nonspontaneous at a higher temperature have a negative  $\Delta H$  and a negative  $\Delta S$ . So in the equation,**

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

**the  $T\Delta S$  term becomes more important as  $T$  increases. That is the absolute magnitude of  $T\Delta S$  becomes larger than the absolute magnitude of  $\Delta H$ .**

- c) Under what circumstances of  $\Delta H$  and  $\Delta S$  will a reaction never be spontaneous?

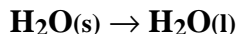
**Reactions that are nonspontaneous at all temperature have a positive  $\Delta H$  and a negative  $\Delta S$ . So in the equation,**

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

**$\Delta G$  is positive at all temperatures, and the reaction is nonspontaneous.**

ICE1.2a. What is the sign for  $\Delta H$  and for  $\Delta S$  when water melts?

**The chemical equation that describes this change is,**



**$\Delta H$  is positive and  $\Delta S$  is positive.**

- b) At what temperature(s) is melting spontaneous? At what temperature(s) is melting of water nonspontaneous?

**Water melts spontaneously above  $0^\circ\text{C}$  but melting is nonspontaneous below  $0^\circ\text{C}$ .**

- c) Does your answer in part a) agree with your answer in part b)?

**Using  $\Delta G = \Delta H - T\Delta S$ , when  $\Delta H$  is + and  $\Delta S$  is + reactions are spontaneous at high temperature (large  $T$ 's) and nonspontaneous at low  $T$ 's. Melting is spontaneous at high  $T$ 's (above  $0^\circ\text{C}$ ) and nonspontaneous at low  $T$ 's (below  $0^\circ\text{C}$ ).**

ICE1.3. For each of the following pairs, choose the substance with the higher entropy (per mole) at a given temperature? In each case include a brief explanation.

- a)  $O_2(g)$  at 5 atm or  $O_2(g)$  at 0.5 atm;

**$O_2(g)$  at 0.5 atm has the higher entropy, since the pressure is lower there will be more space for the molecules to move around in.**

- b)  $Br_2(l)$  or  $Br_2(g)$ ;

**$Br_2(g)$  has the higher entropy compared to  $Br_2(l)$ . When comparing the liquid phase to the gaseous phase for any substance the entropy of the gas phase is always greater.**

- c) 1 mol of  $N_2(g)$  in 22.4 L or 1 mol of  $N_2(g)$  in 2.24 L;

**$N_2(g)$  in 22.4 L has the higher entropy compared to  $N_2(g)$  in 2.24 L. The greater the volume available to the same number of particles the greater the entropy. Again there is more space for the particles to occupy.**

- d)  $CO_2(g)$  or  $CO_2(aq)$ .

**$CO_2(g)$  has the higher entropy compared to  $CO_2(aq)$ . A liquid has a lower entropy compared to a gas, When a gas is dissolved in a liquid the entropy of the mixture is still lower compared to the substance in the gas phase. When a solid dissolves in a solvent the entropy of the solution is generally higher, but not for a gas dissolving in a liquid.**

ICE1.4. Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for each of the following reactions. Also show that in each case  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

- a)  $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

	$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$		
$\Delta H_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-397.7	-436.7	0
$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-296.3	-409.2	0
$S^\circ \left( \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$	143	82.6	205

$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) \\
 &= [2\Delta H_f^\circ (KCl(s)) + 3\Delta H_f^\circ (O_2(g))] - [2\Delta H_f^\circ (KClO_3(s))] \\
 &= \\
 &= [2(-436.7 \text{ kJ}) + 3(0)] - [2(-397.7 \text{ kJ})] \\
 &= -78 \text{ kJ}
 \end{aligned}$$

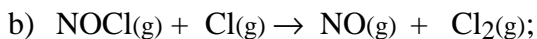
$$\begin{aligned}
\Delta G_{\text{rxn}}^{\circ} &= \Sigma \Delta G_{\text{f}}^{\circ} (\text{products}) - \Sigma \Delta G_{\text{f}}^{\circ} (\text{reactants}) \\
&= [2\Delta G_{\text{f}}^{\circ} \text{KCl}(s) + 3\Delta G_{\text{f}}^{\circ} (\text{O}_2(g))] - [2\Delta G_{\text{f}}^{\circ} (\text{KClO}_3(s))] \\
&= \\
&= [2(-409.2 \text{ kJ}) + 3(0)] - [2(-296.3 \text{ kJ})] \\
&= -225.8 \text{ kJ}
\end{aligned}$$

$$\Delta S_{\text{rxn}}^{\circ} = \Sigma S^{\circ}(\text{products}) - \Sigma S^{\circ}(\text{reactants})$$

$$\Delta S_{\text{rxn}}^{\circ} = [2S^{\circ} \text{KCl}(s) + 3S^{\circ} \text{O}_2(g)] - 2S^{\circ} \text{KClO}_3(s)$$

$$\begin{aligned}
\Delta S_{\text{rxn}}^{\circ} &= [2(82.6 \text{ J K}^{-1}) + 3(205 \text{ J K}^{-1})] - 2(143 \text{ J K}^{-1}) \\
&= 494 \text{ J K}^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta G^{\circ} &= \Delta H^{\circ} - T\Delta S^{\circ} \\
&= -78 \text{ kJ} - 298 \text{ K}(494 \text{ J K}^{-1}) \\
&= -225 \text{ kJ}
\end{aligned}$$



	$\text{NOCl}(g)$	$\text{Cl}(g)$	$\text{NO}(g)$	$\text{Cl}_2(g)$
$\Delta H_{\text{f}}^{\circ} \left( \frac{\text{kJ}}{\text{mol}} \right)$	51.7	122	90.2	0
$\Delta G_{\text{f}}^{\circ} \left( \frac{\text{kJ}}{\text{mol}} \right)$	66.1	106	86.6	0
$S^{\circ} \left( \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$	262	165	211	223

$$\begin{aligned}
\Delta H_{\text{rxn}}^{\circ} &= \Sigma \Delta H_{\text{f}}^{\circ} (\text{products}) - \Sigma \Delta H_{\text{f}}^{\circ} (\text{reactants}) \\
&= [\Delta H_{\text{f}}^{\circ} \text{NO}(g) + \Delta H_{\text{f}}^{\circ} (\text{Cl}_2(g))] - [\Delta H_{\text{f}}^{\circ} (\text{NOCl}(g)) + \Delta H_{\text{f}}^{\circ} (\text{Cl}(g))] \\
&= [90.2 \text{ kJ} + (0)] - [51.7 \text{ kJ} + 122 \text{ kJ}] \\
&= -83.5 \text{ kJ}
\end{aligned}$$

$$\begin{aligned}
\Delta G_{\text{rxn}}^{\circ} &= \Sigma \Delta G_{\text{f}}^{\circ} (\text{products}) - \Sigma \Delta G_{\text{f}}^{\circ} (\text{reactants}) \\
&= [\Delta G_{\text{f}}^{\circ} \text{NO}(g) + \Delta G_{\text{f}}^{\circ} (\text{Cl}_2(g))] - [\Delta G_{\text{f}}^{\circ} (\text{NOCl}(g)) + \Delta G_{\text{f}}^{\circ} (\text{Cl}(g))] \\
&= [86.6 \text{ kJ} + (0)] - [66.1 \text{ kJ} + 106 \text{ kJ}] \\
&= -85.5 \text{ kJ}
\end{aligned}$$

$$\Delta S_{\text{rxn}}^{\circ} = \Sigma S^{\circ}(\text{products}) - \Sigma S^{\circ}(\text{reactants})$$

$$\Delta S_{\text{rxn}}^{\circ} = [S^{\circ} \text{NO}(g) + S^{\circ} \text{Cl}_2(g)] - [S^{\circ} \text{NOCl}(g) + 2S^{\circ} \text{Cl}(g)]$$

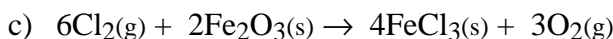
$$\Delta S_{\text{rxn}}^{\circ} = [(211 \text{ J K}^{-1}) + 3(223 \text{ J K}^{-1})] - [(262 \text{ J K}^{-1}) + (165 \text{ J K}^{-1})]$$

$$= +7 \text{ J K}^{-1}$$

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

$$= -83.5 \text{ kJ} - 298 \text{ K}(7 \text{ J K}^{-1})$$

$$= -85.6 \text{ kJ}$$



	$6\text{Cl}_2(g) + 2\text{Fe}_2\text{O}_3(s) \rightarrow 4\text{FeCl}_3(s) + 3\text{O}_2(g)$			
$\Delta H_f^{\circ} \left( \frac{\text{kJ}}{\text{mol}} \right)$	0	-824	-399.5	0
$\Delta G_f^{\circ} \left( \frac{\text{kJ}}{\text{mol}} \right)$	0	-742	-334	0
$S^{\circ} \left( \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$	223	87.4	142	205

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_f^{\circ} (\text{products}) - \Sigma \Delta H_f^{\circ} (\text{reactants})$$

$$= [4\Delta H_f^{\circ} \text{FeCl}_3(s) + 3\Delta H_f^{\circ} (\text{O}_2(g))] - [6\Delta H_f^{\circ} (\text{Cl}_2(g)) + 2\Delta H_f^{\circ} (\text{Fe}_2\text{O}_3(s))]$$

$$= [4(-399.5 \text{ kJ}) + 3(0)] - [2(-824 \text{ kJ}) + 6(0) \text{ kJ}]$$

$$= +50 \text{ kJ}$$

$$\Delta G_{\text{rxn}}^{\circ} = \Sigma \Delta G_f^{\circ} (\text{products}) - \Sigma \Delta G_f^{\circ} (\text{reactants})$$

$$= [4\Delta G_f^{\circ} \text{FeCl}_3(s) + 3\Delta G_f^{\circ} (\text{O}_2(g))] - [6\Delta G_f^{\circ} (\text{Cl}_2(g)) + 2\Delta G_f^{\circ} (\text{Fe}_2\text{O}_3(s))]$$

$$= [4(-334 \text{ kJ}) + 3(0)] - [2(-742 \text{ kJ}) + 6(0) \text{ kJ}]$$

$$= +148 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^{\circ} = \Sigma S^{\circ}(\text{products}) - \Sigma S^{\circ}(\text{reactants})$$

$$\Delta S_{\text{rxn}}^{\circ} = [4S^{\circ} \text{FeCl}_3(s) + 3S^{\circ} \text{O}_2(g)] - [6S^{\circ} \text{Cl}_2(g) + 2S^{\circ} \text{Fe}_2\text{O}_3(s)]$$

$$\Delta S_{\text{rxn}}^{\circ} = [4(142 \text{ J K}^{-1}) + 3(205 \text{ J K}^{-1})] - [6(223 \text{ J K}^{-1}) + 2(87.4 \text{ J K}^{-1})]$$

$$= -330 \text{ J K}^{-1}$$

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

$$= +50 \text{ kJ} - 298 \text{ K}(-330 \text{ J K}^{-1})$$

$$= 148 \text{ kJ}$$

ICE1.5. Write the chemical formula(s) of the product(s) and balance the following reactions. Identify all products phases as either (g)as, (l)iquid, (s)olid or (aq)ueous. Soluble ionic compounds should be written in the form of their component ions.

