

Entropy HW

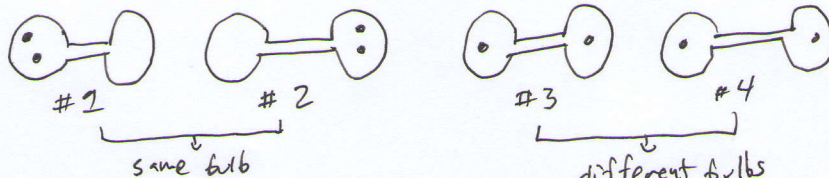
18.1) A spontaneous process is a process in which the entropy of the universe increases, $\Delta S_{\text{universe}} > 0$. Two examples of spontaneous processes are the melting of ice at 50°C and the fall of water down a waterfall. Two examples of non-spontaneous processes are the condensation of water at 1 atm and 200°C and the conversion of graphite to diamond. No outside work or influence is needed to start a spontaneous process.

- 18.2) (a) Salt spontaneously dissolves in hot soup.
 (b) no one spontaneously climbs Mt. Everest.
 (c) perfume spontaneously fills a room.
 (d) separation gas mixtures is non-spontaneous.

8.4) Entropy is a measure of disorder in a system; entropy increases as disorder increases. The typical units of entropy are J/mol K .

- 18.5) (a) $\Delta S_{\text{melt}} > 0$ (e) $\Delta S_{\text{condense}} < 0$
 (b) $\Delta S_{\text{freeze}} < 0$ (f) $\Delta S_{\text{sub}} > 0$
 (c) $\Delta S_{\text{boil}} > 0$ (g) $\Delta S_{\text{dissolve}} > 0$
 (d) $\Delta S_{\text{sep.}} < 0$

8.6) (a) If there are two molecules in the bulbs, there are only two ways in which all the molecules end up in the same bulb:



Since the molecules are in the same bulb $2/4$ times, the probability is $1/2$.

(b) There are still only two ways in which all the molecules end up in the same bulb, but now there are 2^{100} possible configurations of molecules in the bulb (we call these "microstates"). So the probability of all molecules being in the same bulb is $2/2^{100} = 2^{-99} \approx 1.6 \times 10^{-30}$.

(c) Now the probability is $2/2^{6 \times 10^{23}} = 2^{-(6 \times 10^{23} - 1)} \approx 0$.

As we can see, the probability of all molecules being in the same bulb is given by $p(N) = 2^{1-N}$, where $N = \#$ of molecules. As $N \rightarrow$ large numbers, such as moles in macroscopic systems, $p(N) \rightarrow 0$.

18.7) The Second Law of Thermodynamics states that the entropy of the universe increases for all spontaneous processes: $\Delta S_{\text{universe}} > 0$.

18.9) (a) Li(l); solid Li metal is highly ordered as a crystal, whereas the liquid form is much less ordered

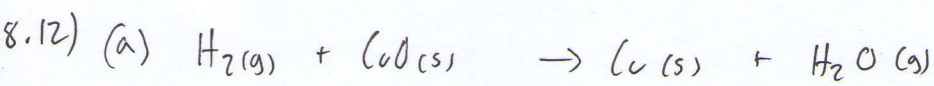
(b) CH₃OCH₃(l); since C₂H₅OH participates in hydrogen bonding, its molecules are less free to move and participate in random, disordered motion

(c) Xe(g); since Xe has more electrons than Ar, its electrons occupy more energy levels and are more disordered

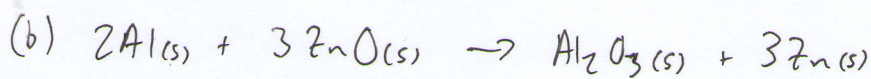
(d) CO₂(g); carbon dioxide can execute more vibrations and has more electrons than the more ordered carbon monoxide

(e) O₃(g); see explanation for CO₂

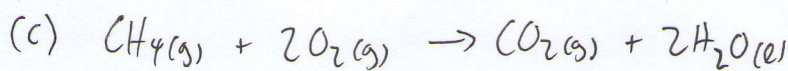
(f) N₂O₄; see explanation for CO₂



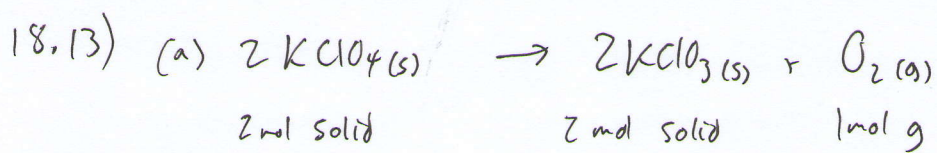
$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= \sum S^{\circ}(\text{products}) - \sum S^{\circ}(\text{reactants}) \\ &= [S^{\circ}(\text{Cu}) + S^{\circ}(\text{H}_2\text{O}(\text{g}))] - [S^{\circ}(\text{H}_2(\text{g})) + S^{\circ}(\text{CuO}(\text{s}))] \\ &= [33.3 \text{ J/mol K} + 188.7 \text{ J/mol K}] - [131.0 \text{ J/mol K} + 43.5 \text{ J/mol K}] \\ \Delta S_{\text{rxn}}^{\circ} &= 47.5 \text{ J/mol K}\end{aligned}$$



$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= [S^{\circ}(\text{Al}_2\text{O}_3(\text{s})) + 3S^{\circ}(\text{Zn}(\text{s}))] - [3S^{\circ}(\text{ZnO}(\text{s})) + 2S^{\circ}(\text{Al}(\text{s}))] \\ &= [50.99 + 3(41.6)] - [3(43.9) + 2(28.3)] \\ \Delta S_{\text{rxn}}^{\circ} &= -12.51 \text{ J/mol K}\end{aligned}$$



$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= [213.6 + 2(69.9)] - [186.2 + 2(205.0)] \\ \Delta S_{\text{rxn}}^{\circ} &= -242.8 \text{ J/mol K}\end{aligned}$$

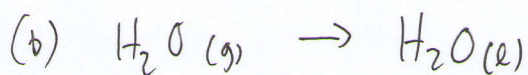


2 mol solid

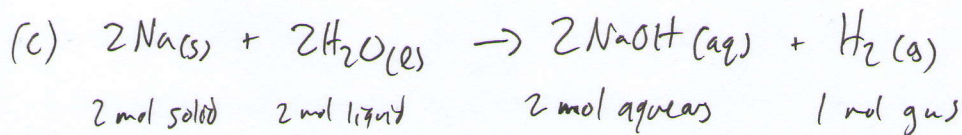
2 mol solid

1 mol g

$$S(\text{gas}) \gg S(\text{solid}) \Rightarrow S(\text{products}) > S(\text{reactants}) \Rightarrow \Delta S_{\text{rxn}} > 0$$



$$S(\text{gas}) > S(\text{liquid}) \Rightarrow S(\text{products}) < S(\text{reactants}) \Rightarrow \Delta S_{\text{rxn}} < 0$$



2 mol solid

2 mol liquid

2 mol aqueous

1 mol gas

$$S(\text{gas}) > S(\text{liquid})$$

$$S(\text{gas}) > S(\text{solid})$$

$$\Rightarrow S(\text{products}) > S(\text{reactants}) \Rightarrow \Delta S_{\text{rxn}} > 0$$

$$S(\text{aqueous}) \overset{\text{usually}}{>} S(\text{pure liquid})$$

$$S(\text{aqueous}) \overset{\text{usually}}{>} S(\text{solid})$$