

## Homework Set #6 (ungraded problems)

6.16 Consider the decomposition of magnesium carbonate:



Calculate the temperature at which the decomposition begins to favor products. Assume that  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are temperature independent. Use the data in Appendix 2 for your calculation.

As discussed in the text for the decomposition of calcium carbonate, a reaction favors the formation of products at equilibrium when

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ < 0$$

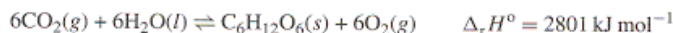
$\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are

$$\begin{aligned}\Delta_r H^\circ &= \Delta_f \bar{H}^\circ [\text{MgO}(s)] + \Delta_f \bar{H}^\circ [\text{CO}_2(g)] - \Delta_f \bar{H}^\circ [\text{MgCO}_3(s)] \\ &= -601.8 \text{ kJ mol}^{-1} + (-393.5 \text{ kJ mol}^{-1}) - (-1095.8 \text{ kJ mol}^{-1}) \\ &= 100.5 \text{ kJ mol}^{-1} \\ \Delta_r S^\circ &= \bar{S}^\circ [\text{MgO}(s)] + \bar{S}^\circ [\text{CO}_2(g)] - \bar{S}^\circ [\text{MgCO}_3(s)] \\ &= 26.78 \text{ J K}^{-1} \text{ mol}^{-1} + 213.6 \text{ J K}^{-1} \text{ mol}^{-1} - 65.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 174.68 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Therefore, for the reaction to begin to favor products,

$$\begin{aligned}\Delta_r H^\circ - T \Delta_r S^\circ &= 100.5 \times 10^3 \text{ J mol}^{-1} - T (174.68 \text{ J K}^{-1} \text{ mol}^{-1}) < 0 \\ T &> \frac{100.5 \times 10^3 \text{ J mol}^{-1}}{174.68 \text{ J K}^{-1} \text{ mol}^{-1}} \\ T &> 575.3 \text{ K}\end{aligned}$$

6.22 Photosynthesis can be represented by



Explain how the equilibrium would be affected by the following changes: (a) the partial pressure of  $\text{CO}_2$  is increased, (b)  $\text{O}_2$  is removed from the mixture, (c)  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose) is removed from the mixture, (d) more water is added, (e) a catalyst is added, (f) the temperature is decreased, and (g) more sunlight shines on the plants.

(a) The equilibrium would shift from left to right.

(b) The equilibrium would shift from left to right.

(c) The equilibrium would be unaffected, since  $\text{C}_6\text{H}_{12}\text{O}_6$  is a solid. (As long as excess solid remains.)

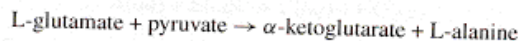
(d) The equilibrium would be unaffected, since water is a liquid. (As long as excess water remains.)

(e) The catalyst has no effect on the position of equilibrium.

(f) The equilibrium would shift from right to left.

(g) Assuming constant temperature, the position of equilibrium is unaffected by the amount of sunlight shining on the plant, although the rate of attaining equilibrium is increased.

6.29 The reaction



is catalyzed by the enzyme L-glutamate-pyruvate aminotransferase. At 300 K, the equilibrium constant for the reaction is 1.11. Predict whether the forward reaction (left to right) will occur spontaneously if the concentrations of the reactants and products are  $[\text{L-glutamate}] = 3.0 \times 10^{-5} \text{ M}$ ,  $[\text{pyruvate}] = 3.3 \times 10^{-4} \text{ M}$ ,  $[\alpha\text{-ketoglutarate}] = 1.6 \times 10^{-2} \text{ M}$ , and  $[\text{L-alanine}] = 6.25 \times 10^{-3} \text{ M}$ .

First calculate  $\Delta_r G^\circ$ , which, together with the reaction quotient, gives  $\Delta_r G$ . The sign of  $\Delta_r G$  determines if the reaction is spontaneous.

$\Delta_r G^\circ$  is related to the equilibrium constant by

$$\Delta_r G^\circ = -RT \ln K = - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln 1.11 = -260.3 \text{ J mol}^{-1}$$

The carbonate ions are supplied by carbon dioxide produced during metabolism. Explain why eggshells are thinner in the summer when the rate of panting by chickens is greater. Suggest a remedy for this situation.

Panting reduces the concentration of  $\text{CO}_2$  because it is exhaled during respiration. Possible solutions include cooling the chickens' environment (to reduce panting) or supplying an additional source of carbonate, such as carbonated drinking water or by adding ground oyster shells to the chicken feed.

6.34 A polypeptide can exist in either the helical or random coil forms. The equilibrium constant for the equilibrium reaction of the helix to the random coil transition is 0.86 at  $40^\circ \text{ C}$  and 0.35 at  $60^\circ \text{ C}$ . Calculate the values of  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  for the reaction.

$\Delta_r H^\circ$  is calculated from the van't Hoff equation.

$$\begin{aligned} \ln \frac{K_2}{K_1} &= \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{0.35}{0.86} &= \frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{313 \text{ K}} - \frac{1}{333 \text{ K}} \right) \\ \Delta_r H^\circ &= -3.90 \times 10^4 \text{ J mol}^{-1} = -3.9 \times 10^4 \text{ J mol}^{-1} \end{aligned}$$

To calculate  $\Delta_r S^\circ$ ,  $\Delta_r G^\circ$  at a particular temperature is needed. The following calculations are carried out using  $40^\circ \text{ C}$ .

$$\Delta_r G^\circ = -RT \ln K = - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (313 \text{ K}) \ln 0.86 = 392 \text{ J mol}^{-1}$$

Assuming  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  to be independent of temperature, the latter can be determined.

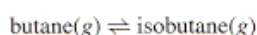
$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{-3.90 \times 10^4 \text{ J mol}^{-1} - 392 \text{ J mol}^{-1}}{313 \text{ K}} = -1.3 \times 10^2 \text{ J K}^{-1} \text{ mol}^{-1}$$

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6.42 Many hydrocarbons exist as structural isomers, which are compounds that have the same molecular formula but different structures. For example, both butane and isobutane have the same molecular formula:  $C_4H_{10}$ . Calculate the mole percent of these molecules in an equilibrium mixture at  $25^\circ C$ , given that the standard Gibbs energy of formation of butane is  $-15.9 \text{ kJ mol}^{-1}$  and that of isobutane is  $-18.0 \text{ kJ mol}^{-1}$ . Does your result support the notion that straight-chain hydrocarbons (that is, hydrocarbons in which the C atoms are joined in a line) are less stable than branch-chain hydrocarbons?

The isomerization process can be expressed as



First calculate  $\Delta_r G^\circ$ , from which the equilibrium constant  $K_p$  is obtained.

$$\begin{aligned}\Delta_r G^\circ &= \Delta_f \bar{G}^\circ [\text{isobutane}] - \Delta_f \bar{G}^\circ [\text{butane}] \\ &= -18.0 \text{ kJ mol}^{-1} - (-15.9 \text{ kJ mol}^{-1}) \\ &= -2.1 \text{ kJ mol}^{-1} \\ \ln K_p &= -\frac{\Delta_r G^\circ}{RT} \\ &= -\frac{-2.1 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 0.848 \\ K_p &= 2.33\end{aligned}$$

The equilibrium constant is a ratio between the pressures of isobutane and butane. The pressure of each gas is proportional to number of moles of gas at constant  $T$  and  $V$ . Therefore,

$$K_p = \frac{P_{\text{isobutane}}}{P_{\text{butane}}} = \frac{n_{\text{isobutane}}}{n_{\text{butane}}} = 2.33$$

According to the above expression, for each mole of butane, there are 2.33 moles of isobutane.

$$\text{Mole percent of isobutane} = \frac{2.33}{3.33} \times 100\% = 70\%$$

$$\text{Mole percent of butane} = 1 - 70\% = 30\%$$

These results support the notion that straight-chain hydrocarbons like butane are less stable than branch-chain hydrocarbons like isobutane.

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