

# Chemistry 2740 Spring 2010 Test 1 Solutions

- Suppose that we have one reaction that, by itself, is not thermodynamically allowed. If we add a second reaction that removes one of the products of the first, and if the overall free energy change for the two reactions put together is negative, then the first reaction can occur. We say in these cases that we have coupled reactions.
  - In indirect calorimetry, we measure gas exchange in a living organism, and perhaps also analyze urine. We use these measurements to estimate the energy used by the organism based on the known stoichiometry of oxygen used, carbon dioxide generated and urea generated in metabolizing different storage compounds (fat, carbohydrates, protein), and on the energy released in these metabolic processes.
  - A microstate (microscopic state) is an arrangement of the components of a system (including the energy stored in the molecules) that is consistent with a given macroscopic state.
  - $\Delta S$  for a reaction between thermodynamic equilibrium states approaches zero as  $T$  approaches zero, i.e. the entropy of a thermodynamic equilibrium state approaches a constant as  $T \rightarrow 0$ .
  - The vapor pressure of a compound is the equilibrium pressure of its vapor over a given condensed phase (solid or liquid) at a particular temperature.
- This is a simple heat balance:

$$\begin{aligned} q = 0 &= \left\{ \begin{array}{l} \text{heat of} \\ \text{reaction} \end{array} \right\} + \left\{ \begin{array}{l} \text{warming} \\ \text{of cell} \end{array} \right\} \\ &= \left\{ \begin{array}{l} \text{heat generated} \\ \text{per hour} \end{array} \right\} \times t + \left\{ \begin{array}{l} \text{warming} \\ \text{of cell} \end{array} \right\} \\ &= (-30.88 \times 10^3 \text{ J/mol})(7 \times 10^{-13} \text{ mol/h})t + (10^{-11} \text{ L})(1000 \text{ g/L})(4.2 \text{ J K}^{-1} \text{ g}^{-1})(5 \text{ K}). \\ \therefore t &= \frac{(10^{-11} \text{ L})(1000 \text{ g/L})(4.2 \text{ J K}^{-1} \text{ g}^{-1})(5 \text{ K})}{(30.88 \times 10^3 \text{ J/mol})(7 \times 10^{-13} \text{ mol/h})} \\ &= 9.7 \text{ h.} \end{aligned}$$

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$$\begin{aligned} \Delta_r G_m^\circ &= -RT \ln K \\ &= -(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(0.087) \\ &= 6.05 \text{ kJ/mol.} \\ \Delta_r G_m^\circ &= \Delta_f G^\circ(\text{aq}) - \Delta_f G^\circ(\text{g}) \\ \therefore \Delta_f G^\circ(\text{aq}) &= \Delta_r G_m^\circ + \Delta_f G^\circ(\text{g}) \\ &= 6.05 + (-33.33) \text{ kJ/mol} = -27.28 \text{ kJ/mol.} \end{aligned}$$

(b)

$$\begin{aligned}\text{slope} &= -\Delta_r H_m^\circ / R \\ \therefore \Delta_r H^\circ &= -R(\text{slope}) \\ &= -(8.314\,472 \text{ J K}^{-1}\text{mol}^{-1})(2100 \text{ K}) \\ &= -17.46 \text{ kJ/mol.} \\ \Delta_r H_m^\circ &= \Delta_f H^\circ(\text{aq}) - \Delta_f H^\circ(\text{g}) \\ \therefore \Delta_f H^\circ(\text{aq}) &= \Delta_r H_m^\circ + \Delta_f H^\circ(\text{g}) \\ &= -17.46 + (-20.50) \text{ kJ/mol} = -37.96 \text{ kJ/mol.}\end{aligned}$$

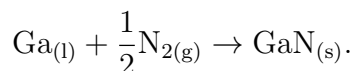
(c)

$$\begin{aligned}\Delta_r G_m^\circ &= \Delta_r H_m^\circ - T\Delta_r S_m^\circ \\ \therefore \Delta_r S_m^\circ &= \frac{\Delta_r H_m^\circ - \Delta_r G_m^\circ}{T} \\ &= \frac{-17.46 - 6.05 \text{ kJ/mol}}{298.15 \text{ K}} = -78.9 \text{ J K}^{-1}\text{mol}^{-1}. \\ \Delta_r S_m^\circ &= S_m^\circ(\text{aq}) - S_m^\circ(\text{g}) \\ \therefore S_m^\circ(\text{aq}) &= \Delta_r S_m^\circ + S_m^\circ(\text{g}) \\ &= -78.9 + 205.77 \text{ J K}^{-1}\text{mol}^{-1} = 126.9 \text{ J K}^{-1}\text{mol}^{-1}.\end{aligned}$$

4. (a)  $\Delta_f G^\circ = \Delta_f H^\circ - T\Delta_f S^\circ$ . By comparison,  $\Delta_f H^\circ = -131.53 \text{ kJ/mol}$ .  
(b) This is  $-\Delta_f S^\circ$ , where  $\Delta_f S^\circ$  is the standard entropy change of formation, i.e. the entropy change in the formation of GaN from its elements under standard conditions.  
(c) As long as  $\Delta_f G^\circ < 0$ , GaN is stable with respect to its elements under standard conditions, i.e. at 1 bar  $\text{N}_2$ . It will become unstable when  $\Delta_f G^\circ > 0$ . The dividing line between the two is  $\Delta_f G^\circ = 0$ , i.e.

$$T = \frac{131\,530 \text{ J/mol}}{117.4 \text{ J K}^{-1}\text{mol}^{-1}} = 1120 \text{ K}.$$

- (d) The reasoning here is similar to the reasoning in the previous part, except that we want  $\Delta_f G = 0$ . The formation reaction is



The free energy of formation of GaN therefore depends on the pressure of  $\text{N}_2$  as follows:

$$\begin{aligned}\Delta_f G &= \Delta_f G^\circ + RT \ln \left( \frac{1}{a_{\text{N}_2}^{1/2}} \right) \\ &= -131\,530 + 117.4T + (8.314\,472 \text{ J K}^{-1}\text{mol}^{-1})T \ln \left( \frac{1}{20^{1/2}} \right) \\ &= -131\,530 + 104.9T.\end{aligned}$$

If we set this equation equal to zero and solve for  $T$ , we get

$$T = \frac{131\,530 \text{ J/mol}}{104.9 \text{ J K}^{-1}\text{mol}^{-1}} = 1253 \text{ K.}$$

Looking at the formation reaction, Le Chatelier's principle would predict that increasing the pressure of nitrogen should shift the equilibrium toward the products, i.e. make GaN stable over a wider temperature range or, in other words, raise the decomposition temperature, which is exactly what we observe.