



Pre-Health Post-Baccalaureate Program Study Guide and Practice Problems

Course: CHM2046

Textbook Chapter: 20 (Silberberg 6e)

Topics Covered: Thermodynamics

1. Where We've Been, and Where We're Going

In the last several chapters, we've talked about systems in equilibrium and explored reaction rates. We have said that reactions are either driven towards the products or reactants, and that equilibrium is the position at which the forward rate equals the backward rate.

But what kind of chemical processes drive reactions and determine which side of a reaction is favored? What does changing energy levels have to do with all of this? What does it mean for a reaction to be spontaneous?

In this chapter, we will explore thermodynamics, which answers these questions.

2. The Quest to Determine the Direction of Spontaneous Change

The First Law of Thermodynamics, also called the Law of Conservation of Energy, and states that a system's internal energy (E) is dependent upon how much heat (q) and work (w) are absorbed or released:

$$\Delta E = q + w$$

This law also informs us of an important reciprocal relationship. Any change of internal energy system comes at the expense of an negative external energy change. Put another way, the surroundings must lose energy in order for the system to gain energy, since energy cannot be created or destroyed:

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$$
$$(q + w)_{\text{sys}} = -(q + w)_{\text{surr}}$$

This principle only communicates that a system can gain or release energy to it's surroundings.

Let's also revisit another topic: enthalpy change (ΔH). Enthalpy changes tells us only if a reaction is endothermic or exothermic, that is, if a reaction requires or gives off heat. Depending on reaction conditions, reactions with both positive and negative values for enthalpy change can be

spontaneous.

Therefore, neither the First Law nor enthalpy change can determine the direction of spontaneous change of a reaction.

3. Introducing Entropy

In order to understand spontaneity, we must first understand the Second Law of Thermodynamics. The Second Law is all about entropy (S), which is usually defined as randomness or disorder. This law tells us that the entropy of the universe is always increasing, but it does not however, mean that the entropy of the system is always increasing:

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = \Delta S_{\text{univ}} > 0$$

Entropy is extensive, so you will often see it as S° , or standard molar entropy, which defines entropy in terms of J/mol*K.

As temperature (T) increases (including when a substance changes from solid to liquid to gas), standard molar entropy increases.

As a substance is dissolved in water (**except** during complex ion formation and dissolved gasses), standard molar entropy increases.

As we move down a periodic table group, standard molar entropy increases.

As chemical complexity increases, standard molar entropy increases

Entropy of the surroundings can be mathematically related to enthalpy change of the system and temperature:

$$\Delta S_{\text{surr}} = - \frac{\Delta H_{\text{sys}}}{T}$$

At equilibrium, no further net change occurs, therefore:

$$\Delta S_{\text{univ}} = 0$$

5. Gibb's Free Energy.

Note: This topic is incredibly important!

Gibbs Free Energy (ΔG) is determined by the enthalpy of the system, temperature, and entropy of the system:

$$\Delta G_{\text{sys}}^{\circ} = \Delta H_{\text{sys}}^{\circ} - T\Delta S_{\text{sys}}^{\circ}$$

The sign of ΔG informs us whether a reaction is spontaneous, at equilibrium, or non-spontaneous:

$\Delta G < 0$... spontaneous (energy available to be released)

$\Delta G = 0$... at equilibrium

$\Delta G > 0$... non-spontaneous (energy must be added)

	$\Delta H^{\circ} < 0$	$\Delta H^{\circ} > 0$
$\Delta S^{\circ} > 0$	Spontaneous	Spontaneous @ high temps
$\Delta S^{\circ} < 0$	Spontaneous @ low temps	Non-spontaneous

Let's now relate this topic to K and Q:

$$\Delta G = RT \ln \frac{Q}{K} = RT (\ln Q - \ln K)$$

We will once again use our "King before Queen" mnemonic:

According to the above equation, what makes ΔG negative, and the reaction spontaneous? ΔG is negative when $\ln(Q/K)$ is negative. $\ln(Q/K)$ is negative when $Q < K$. So...

If $K > Q$, the reaction will proceed spontaneously to the right, or non-spontaneously to the left.

According to the above equation, what makes ΔG positive, and the reaction non-spontaneous? ΔG is positive when $\ln(Q/K)$ is positive. $\ln(Q/K)$ is positive when $Q > K$. So...

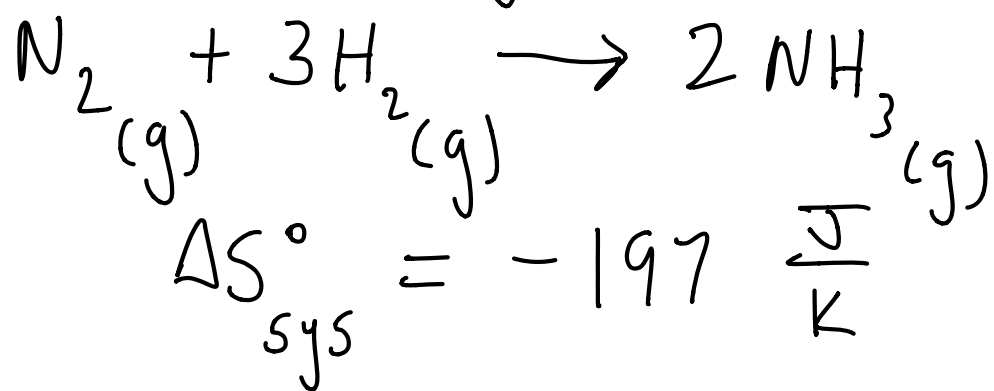
If $K < Q$, the reaction will proceed spontaneously to the left, or non-spontaneously to the right.

According to the above equation, what makes ΔG zero, and the reaction at equilibrium? ΔG is zero when $\ln(Q/K)$ is zero. $\ln(Q/K)$ is zero when $Q = K$. So...

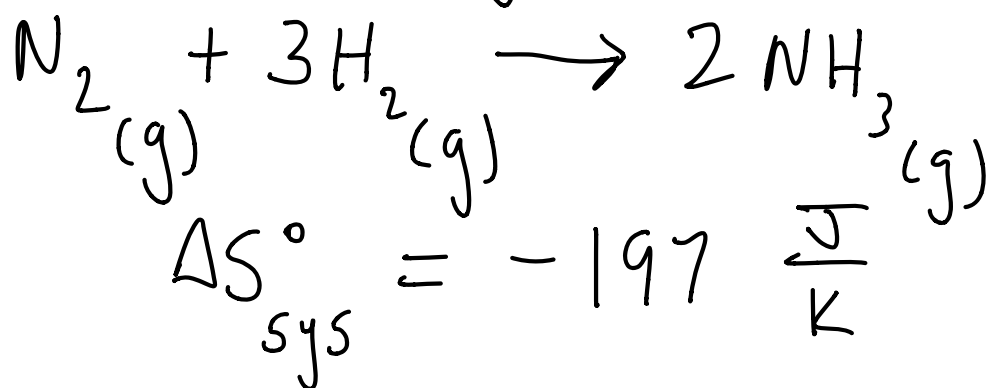
If $K = Q$, the reaction will not proceed either direction (but we already knew this one!).

Problems:

① For the following reaction at 298 K, calculate ΔS_{univ} and determine if the reaction proceeds spontaneously:



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$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}}^{\circ} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}}^{\circ} + \left(-\frac{\Delta H_{\text{sys}}^{\circ}}{T} \right)$$

$$\Delta S_{\text{univ}} = -197 \frac{\text{J}}{\text{K}} + \left(-\frac{-91.8 \cancel{\text{kJ}} \times \frac{1000 \text{J}}{1 \cancel{\text{kJ}}}}{298 \text{K}} \right)$$

$$\Delta S_{\text{univ}} = -197 \frac{\text{J}}{\text{K}} + 308 \frac{\text{J}}{\text{K}} = 111 \frac{\text{J}}{\text{K}}$$

$111 \frac{\text{J}}{\text{K}} > 0$, \therefore happens spontaneously at 298 K

② Calculate the $\Delta S_{\text{rxn}}^{\circ}$ for the combustion of 1 mol of propane, C_3H_8 , at 25°C .

$$S^{\circ}_{\text{C}_3\text{H}_8} = 269.9 \frac{\text{J}}{\text{mol K}}$$

$$S^{\circ}_{\text{O}_2} = 205.0 \frac{\text{J}}{\text{mol K}}$$

$$S^{\circ}_{\text{CO}_2} = 213.7 \frac{\text{J}}{\text{mol K}}$$

$$S^{\circ}_{\text{H}_2\text{O}} = 69.9 \frac{\text{J}}{\text{mol K}}$$

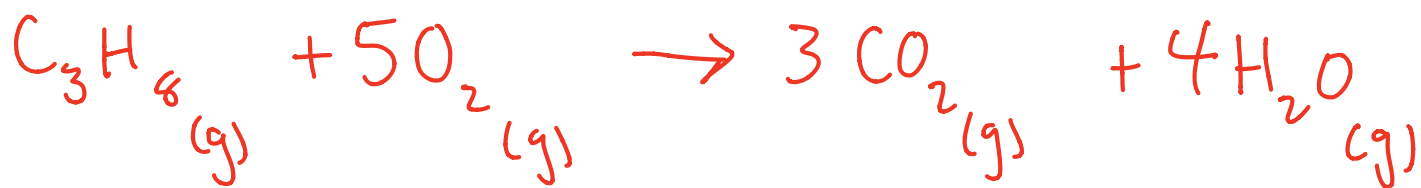
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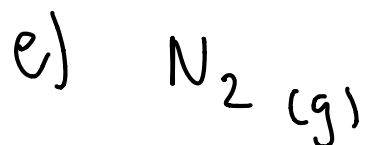
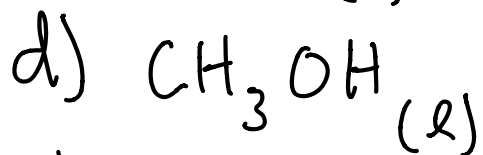
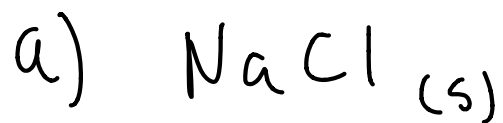
$$S^\circ_{\text{H}_2\text{O}} = 69.9 \frac{\text{J}}{\text{mol K}}$$



$$\Delta S^\circ_{\text{rxn}} = \left[(3 \times 213.7) + (4 \times 69.9) \right] - \left[269.9 + (5 \times 69.9) \right]$$

$$\Delta S^\circ_{\text{rxn}} = -374 \frac{\text{J}}{\text{K}}$$

③ For which of the following would the ΔS° value be negative upon dissolution in water?

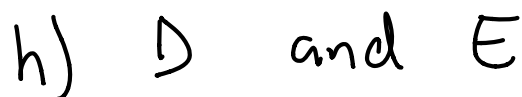
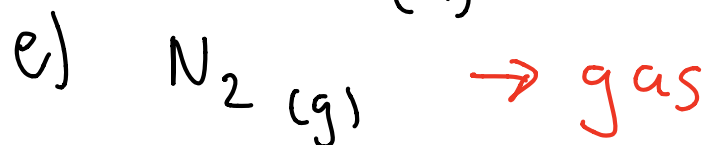
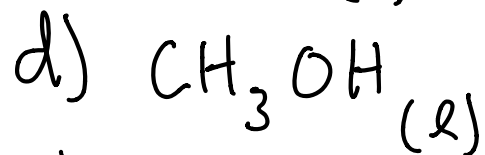
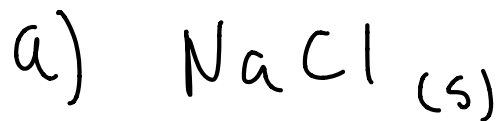


f) A and C

g) B and E

h) D and E

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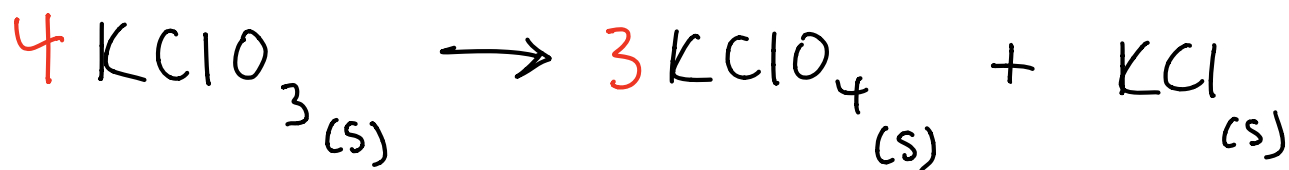


④ Calculate the $\Delta G^\circ_{\text{rxn}}$ at 25°C for the following reaction:



	ΔH°	ΔS°
$\text{KClO}_3(s)$	$-397.7 \frac{\text{kJ}}{\text{mol}}$	$143.1 \frac{\text{J}}{\text{mol}\cdot\text{K}}$
$\text{KClO}_4(s)$	$-432.8 \frac{\text{kJ}}{\text{mol}}$	$151.0 \frac{\text{J}}{\text{mol}\cdot\text{K}}$
$\text{KCl}(s)$	$-436.7 \frac{\text{kJ}}{\text{mol}}$	$82.6 \frac{\text{J}}{\text{mol}\cdot\text{K}}$

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$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$$

$$\Delta G^\circ_{\text{rxn}} = \left(\sum m \Delta H^\circ_p - \sum n \Delta H^\circ_r \right) - \left[T \left(\sum m \Delta S^\circ_p - \sum n \Delta S^\circ_r \right) \right]$$

$$\Delta G^\circ_{\text{rxn}} = \left(\left[(3 \times -432.8) + (-436.7) \right] - (4 \times -397.7) \right) \\ - \left[298 \left(\left[(3 \times 151.0) + (82.6) \right] - (4 \times 143.1) \right) \right]$$

$$\Delta G^\circ_{\text{rxn}} = -133 \text{ kJ}$$

Don't let the messiness of the math mess with you!