Midterm 2a Problems

February 28, 2022

1. **Entropy** Does the entropy of the system/reaction mixture increase, decrease, or stay the same in the following processes? Briefly explain your answer in each case.

a) Haber-Bosch synthesis of ammonia

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

Entropy decreases since there are fewer moles of products than reactants

b) Isomerization of neopentance (2,2-dimethylpropane) to n-pentane

Entropy increases since n-pentane has greater flexibility; draw the Lewis structures

c) Isothermal compression of an ideal gas

Entropy decreases since the volume decreases

$$\Delta S = R \ln \frac{V_f}{V_i}$$

where V_f and V_i are the final and initial states, respectively.

d) Mixing of fixed amounts of two chemically different ideal gases at constant temperature, total pressure, and total volume

Entropy increases since partial pressures of the gases decreases upon mixing.

2. **Essay Question: Gibbs Free Energy** Explain in a few sentences why the Gibbs free energy is a central quantity in chemical thermodynamics. What type(s) of information can be obtained from the Gibbs free energy change of a process? Name at least two methods for determining the Gibbs free energy of a chemical reaction experimentally, computationally, or using tabulated data.

Delta G also gives the amount of available work (at constant pressure). It also determines the equilibrium constant and provides the direction or "driving force" for a reaction to achieve equilibrium. Two ways of determining the Gibbs free energy of a reaction:

1. $\Delta G = \Delta H_r^\circ - T\Delta S_r^\circ$ where ΔH_r° and ΔS_r° are the standard enthalpy and standard entropy of reaction. These are determined from tabulated standard enthalpy and standard entropy of formation. T is the temperature
2. $\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ(P_i) - \sum_i \nu_i(R_i)\Delta G_f^\circ(R_i)$ using tabulated standard free energies of formation ΔG_f° and cofficients of the reaction ν

3. **Equilibrium Constants** Determine K_c at 25°C for the reaction,

$$N_2\,(g) + O_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NOCl\,(g),$$

given the following data set at 25°C. Report result to 2 significant figures.

$$N_2\,(g) + 2\,O_2\,(g) \rightleftharpoons 2\,NO_2(g) \quad K_p = 1.0 \times 10^{-18}\,\text{atm}^{-1}$$
$$2\,NOCl\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2Cl(g) \quad K_p = 1.21 \times 10^{4}\,\text{atm}^{-1}$$
$$2\,NO_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NO_2Cl(g) \quad K_p = 9.0 \times 10^{-2}\,\text{atm}^{-1}$$

Invert the second equation and take the product. The overall $K_p = 7.4 \times 10^{-24}$ atm^{-1} and $K_c = 3.0 \times 10^{-25}$ M^{-1}

4. **Van't Hoff Equation** In the gas phase, nitrosyl chloride NOCl is in chemical equilibrium with its dissociation products, nitrogen monoxide and chlorine gas.

	ΔH_f° (kJ/mol)	ΔS° (J/(mol K))
NO	90.29	210.76
ClNO	51.71	261.68
Cl_2		223.08

Table 1: Thermochemical data at standard conditions.

a) Formulate the balanced chemical equation including states.

$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$

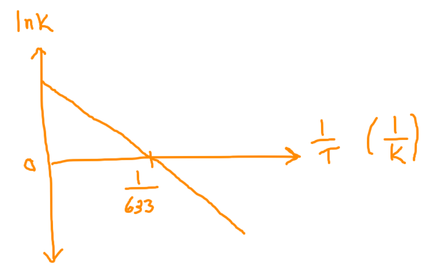
b) Using the thermochemical data from Table 1, estimate the temperature T_c at which the equilibrium constant K equals 1.

Use the following equation

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

and determine $\Delta H^\circ = 77.16$ kJ/mol and $\Delta S^\circ = 121.96$ J/(mol K). The temperature at which $K = 1$ is 633 K.

c) Qualitatively plot $\ln K$ as a function of $1/T$ based on your results from (b). Label your axes.



5. **Statistical Thermodynamics** 2.5 mol of ethyne (a.k.a. acetylene, C_2H_2) gas are kept in a 1 L steel cylinder. Assume ideal behavor.

a) Determine the total entalpy of the sample at 300 K.

$U = H - PV$ at constant pressure P and H is the total enthalpy. Quadratic degree of freedom $f_q = 5$. Hence, $U = \frac{5}{2}nRT$ and using ideal gas $PV = nRT$

$$\begin{aligned} H =& U + PV \\ =& U + nRT \\ =& \frac{5}{2}nRT + nRT \\ =& (\frac{5}{2} + 1)(2.5 \times 0.08206 \times 300) \\ =& 215.4075 \text{ L atm} = 21.8 \text{ kJ} \end{aligned}$$

b) The pressure of the sample is doubled by reducing the volume to 0.5 L. The temperature is kept constant. Determine the total enthalpy.

21.8 kJ

c) Estimate the root mean square (rms) velocity of the ethyne molecules in m/s at 300 K. The mass of a single ethyne molecule is 4.324×10^{-26} kg.

$$\begin{aligned} \frac{1}{2}mv_{\text{rms}}^2 =& \frac{3}{2}kT \\ v_{\text{rms}} =& \sqrt{\frac{3}{4.324 \times 10^{-26}}(1.3806 \times 10^{-23})(300)} \\ v_{\text{rms}} =& 536 \text{ m/s} \end{aligned}$$

d) Determine the entropy change when the original gas sample is heated from 300 K to 800 K.

Determing $C_v = f_q \frac{1}{2} nR$

$$\Delta S = C_v \ln \frac{T_f}{T_i}$$
$$= 51.0 \text{ J/K}$$

e) Ethyne has a standard free energy of formation of 209.9 kJ/mol. Why is it not smart to heat a pressurized steel cylinder containing ethyne?

The formation of C_2H_2 has chemical formula 2 C(s) + H_2(g)$\rightleftharpoons$ C_2H_2(g). It is spontaneous for the decomposition of C_2H_2(g) into the elements and releases free energy. H_2 is highly explosive.