

Ch14 Spring 2024
Problem set 1
due April 11, 2024

unless otherwise stated, assume $T = 25^\circ\text{C}$ and that activities = concentrations.

unless otherwise specified, give answers to 3 significant figures.

1

1. (30 pts total) At 25°C and 1 atm, the standard free energies (G°_f) of formation of benzene in the liquid and gas phase have the following values:

phase	G°_f (kJmol^{-1})
liquid	124.5
gas	129.7

1.1

- 1a. (10 pts) Which phase (liquid or gas) is more stable under these conditions? Explain briefly (12 sentences)

The liquid phase, because it has the lower free energy of formation.

1.2

- 1b. (10 pts) Calculate the vapor pressure of benzene under these conditions. Express your answer in both Pa and mmHg. ($1 \text{ atm} = 101325 \text{ Pa} =$

760 mmHg)

We can use the formula:

$$\Delta G = -RT \ln P \quad (1)$$

to find the vapor pressure of benzene. We can rearrange the formula to solve for P :

$$P = e^{-\frac{\Delta G}{RT}} \quad (2)$$

The change in free energy is given by:

$$\Delta G = G_{\text{gas}} - G_{\text{liquid}} = 129.7 - 124.5 = 5.2 \text{ kJ/mol} = 5.2 \times 10^3 \text{ J/mol} \quad (3)$$

Substituting the values into the formula, we get:

$$P_{\text{atm}} = 0.123 \text{ atm} = 12400 \text{ Pa} = 93.2 \text{ mm Hg} \quad (4)$$

```
1 import math
2
3 # Constants
4 delta_G = 5.2 * 1000 # Change in free energy, in J/mol
5 R = 8.314 # Universal gas constant, in J/(molxK)
6 T = 298 # Temperature, in K
7
8 # Calculating vapor pressure in atm
9 P_atm = math.exp(-delta_G / (R * T))
10
11 # Conversion factors
12 Pa_per_atm = 101325 # Pascal per atm
13 mmHg_per_atm = 760 # mm Hg per atm
14
15 # Converting to Pa and mm Hg
16 P_Pa = P_atm * Pa_per_atm
17 P_mmHg = P_atm * mmHg_per_atm
18
19 P_atm, P_Pa, P_mmHg
```

1.3

1c. (10 pts) If 10mls of liquid benzene are placed in an evacuated 1 liter flask, how much benzene (in milliliters) will evaporate to reach equilibrium at 25°C ? i.e. - how many mls of liquid benzene must evaporate to achieve the vapor pressure calculated in problem 1 b ? If you are unsure of your answer to 1 b, use $P = 100 \text{ mmHg}$ (accurate to within 10%)

Other potentially useful information: the molecular weight of benzene is 78.11gmmol^{-1} and the density is 0.876gmml^{-1} (876 kg m^{-3}). Assume ideal gas behavior; values for the gas constant R are $8.3144\text{ J mol}^{-1}\text{ K}^{-1}$ and $0.08206\text{ liter atm mol}^{-1}\text{ K}^{-1}$, in SI and non-SI units, respectively. You may neglect the volume of the liquid in working this problem (ie - you may assume that the volume of the gas phase is 1 L).

Our algorithm to solve this problem is as follows:

1. Calculate the number of moles of benzene in the gas phase at equilibrium.
2. Calculate the mass of evaporated benzene.
3. Calculate the volume of benzene that evaporated.

I chose to use the value of 100 mm Hg for the vapor pressure in this calculation. To achieve the vapor pressure given in the instructions, 0.480 mL of liquid benzene must evaporate.

```

1 # Given data
2 P_mmHg = 100 # Vapor pressure in mm Hg
3 P_atm = P_mmHg / 760 # Converting pressure to atm
4 V_L = 1 # Volume in liters
5 R_L_atm_per_mol_K = 0.08206 # Gas constant in liter atm per
   mol K
6 T_C = 25 # Temperature in Celsius
7 T_K = T_C + 273.15 # Converting temperature to Kelvin
8
9 # Calculating moles of benzene vapor at equilibrium using the
   ideal gas law
10 n_moles = (P_atm * V_L) / (R_L_atm_per_mol_K * T_K)
11
12 # Given molecular weight and density of benzene
13 molecular_weight_benzene = 78.11 # g/mol
14 density_benzene_g_per_ml = 0.876 # g/ml
15
16 # Calculating mass of evaporated benzene
17 mass_evaporated_g = n_moles * molecular_weight_benzene
18
19 # Calculating volume of evaporated benzene in ml
20 volume_evaporated_ml = mass_evaporated_g /
   density_benzene_g_per_ml
21
22 n_moles, mass_evaporated_g, volume_evaporated_ml

```

2

2. (40 pts total) The hydrolysis of adenosine triphosphate (ATP) to form ADP + inorganic phosphate (Pi) : $ATP \rightarrow ADP + P_i$, is an important reaction in bioenergetics. Under standard conditions 25°C and 1 atm, $\Delta G^\circ = -30 \text{ kJ mol}^{-1}$.

2.1

- 2a. (10 pts) What is K_{eq} for this reaction?

We can use the formula:

$$\Delta G = -RT \ln K_{eq} \quad (5)$$

to find the equilibrium constant for the reaction. We can rearrange the formula to solve for K_{eq} :

$$K_{eq} = e^{-\frac{\Delta G}{RT}} \quad (6)$$

Substituting the values into the formula, we get:

$$K_{eq} = 1.80 \times 10^5 \quad (7)$$

```
1 # Given data
2 delta_G_kJ_per_mol = -30 # Change in free energy, in kJ/mol
3 delta_G_J_per_mol = delta_G_kJ_per_mol * 1000 # Convert kJ/
  mol to J/mol
4 R = 8.314 # Universal gas constant, in J/(molxK)
5 T_C = 25 # Temperature in Celsius
6 T_K = T_C + 273.15 # Converting temperature to Kelvin
7
8 # Calculating Keq
9 K_eq = math.exp(-delta_G_J_per_mol / (R * T_K))
10
11 K_eq
```

2.2

- 2b. (10 pts) Under physiological conditions, the concentration of ADP is kept to very low values in the cell by continual rephosphorylation to form ATP. What is ΔG under physiological conditions, when $(ATP) = 10\text{mM}$, $(ADP) =$

10 μ M and (Pi) = 10mM ?

In order to solve this problem, we want to consider the relationship:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (8)$$

where ΔG is the change in free energy, ΔG° is the standard change in free energy, R is the universal gas constant, T is the temperature, and Q is the reaction quotient. The reaction quotient is given by:

$$Q = \frac{[\text{ADP}][\text{Pi}]}{[\text{ATP}]} \quad (9)$$

Performing this computation, we get:

$$\Delta G = -58.5 \text{ kJ/mol} \quad (10)$$

```
1 # Given data
2 delta_G_zero_J_per_mol = -30000 # Standard free energy
   change in J/mol
3 ATP_concentration_mM = 10 # mM
4 ADP_concentration_uM = 10 # uM
5 Pi_concentration_mM = 10 # mM
6
7 # Convert concentrations to M (mol/L)
8 ATP_concentration_M = ATP_concentration_mM * 10**-3
9 ADP_concentration_M = ADP_concentration_uM * 10**-6
10 Pi_concentration_M = Pi_concentration_mM * 10**-3
11
12 # Calculate Q
13 Q = (ADP_concentration_M * Pi_concentration_M) /
   ATP_concentration_M
14
15 # Calculate Delta G under physiological conditions
16 Delta_G = delta_G_zero_J_per_mol + (R * T_K * math.log(Q))
17
18 Delta_G
```

2.3

2c. (10 pts) Starting with (ATP) = 0mM, (ADP) = 1mM, (Pi) = 1mM, what is the concentration of ATP at equilibrium?

Previously, we calculated the equilibrium constant for the reaction as $1.80 \times$

10^5 . We can use this value to calculate the concentration of ATP at equilibrium. The reaction quotient Q is given by:

$$Q = \frac{[\text{ADP}][\text{Pi}]}{[\text{ATP}]} \quad (11)$$

At equilibrium, $Q = K_{\text{eq}}$. We can rearrange the formula to solve for $[\text{ATP}]$:

$$[\text{ATP}] = \frac{[\text{ADP}][\text{Pi}]}{K_{\text{eq}}} \quad (12)$$

Substituting the values into the formula, we get:

$$[\text{ATP}] = 5.55 \times 10^{-12} \text{ M} \quad (13)$$

```

1 # Recalculating ATP concentration at equilibrium
2 ADP_concentration_M = 1e-3 # M
3 Pi_concentration_M = 1e-3 # M
4
5 # Calculating ATP concentration at equilibrium using the
  corrected formula
6 ATP_concentration_at_equilibrium_M = (ADP_concentration_M *
  Pi_concentration_M) / K_eq_value
7
8 ATP_concentration_at_equilibrium_M

```

2.4

2d. (10 pts) Starting with $(\text{ATP}) = 0\text{mM}$, $(\text{ADP}) = 1\text{mM}$, $(\text{Pi}) = 1000\text{mM}$, what is the concentration of ATP at equilibrium?

Note: the equilibrium for ATP hydrolysis greatly favors the products ADP and Pi, so that the final product concentrations ((ADP) and (Pi)) may be equated to the initial product concentrations for problems 2c and 2 d.

Using the similar procedure as was done previously:

$$[\text{ATP}] = 5.55 \times 10^{-9} \text{ M} \quad (14)$$

```

1 # Updated initial conditions for problem 2d
2 Pi_concentration_M_updated = 1000e-3 # M, converting from mM
  to M

```

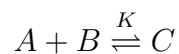
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3
4 # Recalculating ATP concentration at equilibrium with updated
   Pi concentration
5 ATP_concentration_at_equilibrium_M_updated = (
   ADP_concentration_M * Pi_concentration_M_updated) /
   K_eq_value
6
7 ATP_concentration_at_equilibrium_M_updated

```

3

3. (10 pts) The following reaction has an equilibrium constant $K = 10$ at 25°C (when concentrations are defined using the Molar (moles/liter) solution convention)



What are the concentrations of (A) , (B) and (C) at equilibrium, starting with $(A) = (B) = 0.0\text{M}$ and $(C) = 0.1\text{M}$?

Using this information, we find:

$$\boxed{[A] = [B] = 0.062 \text{ M}, \quad [C] = 0.038 \text{ M}} \quad (15)$$

```

1 from sympy import symbols, Eq, solve
2
3 # Define symbol
4 x = symbols('x')
5
6 # Given data
7 K = 10 # Equilibrium constant
8 initial_C = 0.1 # Initial concentration of C in M
9
10 # Equilibrium expressions
11 # [C] = initial_C - x, [A] = x, [B] = x
12
13 # Equilibrium constant expression
14 equation = Eq(K, (initial_C - x) / (x**2))
15
16 # Solve for x
17 x_solution = solve(equation, x)

```

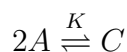
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18
19 # Filter out the negative solution since concentration cannot
    be negative
20 x_equilibrium = [sol for sol in x_solution if sol > 0]
21
22 # Calculate equilibrium concentrations
23 A_eq = B_eq = x_equilibrium[0]
24 C_eq = initial_C - x_equilibrium[0]
25
26 A_eq, B_eq, C_eq

```

4

4. (10 pts) The following reaction has an equilibrium constant $K = 10$ at 25°C (when concentrations are defined using the Molar (moles/liter) solution convention)



What are the concentrations of (A) and (C) at equilibrium, starting with (A) = 0.0M and (C) = 0.1 M ?

Because the stoichiometry of the reaction is different, the expression for the equilibrium constant is:

$$K = \frac{[C]}{[A]^2} \quad (16)$$

Using this information, we find:

$$\boxed{[A] = 0.078 \text{ M}, \quad [C] = 0.061 \text{ M}} \quad (17)$$

```

1 # Define a new symbol for x representing the change for this
    reaction
2 x_2A_to_C = symbols('x')
3
4 # Given data for the new problem
5 K_2A_to_C = 10 # Equilibrium constant
6 initial_C_2A_to_C = 0.1 # Initial concentration of C in M
7
8 # Equilibrium expressions for the reaction 2A <-> C
9 # [C] = initial_C - x, [A] = 2x

```


The equilibrium constant is given by:

$$K = \frac{P_{\text{dimer}}}{P_{\text{monomer}}^2} \quad (19)$$

Substituting the values into the formula, we get:

$$P_{\text{monomer}} = 0.498 \text{ atm}, \quad P_{\text{dimer}} = 0.502 \text{ atm} \quad (20)$$

```

1 # Define symbol for x, representing the partial pressure of
  the monomer
2 x = symbols('x', real=True, positive=True)
3
4 # Given data
5 K_value = 2.02 # Equilibrium constant
6 total_pressure = 1 # Total pressure in atm
7
8 # Equilibrium expressions
9 # For monomer (A), P_monomer = x
10 # For dimer (A2), P_dimer = total_pressure - x
11
12 # Equilibrium constant expression K = P_dimer / P_monomer^2
13 equation = Eq(K_value, (total_pressure - x) / x**2)
14
15 # Solve for x (P_monomer)
16 x_solution = solve(equation, x)
17
18 # Filter out the negative and non-real solutions since
  pressure cannot be negative or non-real
19 x_real_solutions = [sol.evalf() for sol in x_solution if sol.
  is_real and sol > 0]
20
21 # Select the first solution (there should only be one
  positive real solution in this physical context)
22 P_monomer_atm = x_real_solutions[0]
23
24 # Calculate P_dimer using the total pressure and the
  calculated P_monomer
25 P_dimer_atm = total_pressure - P_monomer_atm
26
27 P_monomer_atm, P_dimer_atm

```