

## 06I: Problem Related to the Chemical Potential

### Practice Homework Problems

#### 1. Definitions

- What are the units for the Chemical Potential?
- Please give the rationale for your answer to above.
- Generally we write  $\mu_{species} = \mu_{species}^{std\ state} + RT \ln a_{species}$ . The chemical potential of an idea gas is given by (for example oxygen)  $\mu_{O_2} = RT \ln p_{O_2}$  where the partial pressure of oxygen is expressed in atmospheres. What is the standard state in this instance.

#### 2. Activity

Consider a saturated solution of brine (salt crystals are in equilibrium with water in the solution).

- (i) Is the following equation correct, and if yes the why:  $\mu_{NaCl}^{crystal} = \mu_{NaCl}^{water\ solution}$  ?
- (ii) The addition of salt reduces the activity of H<sub>2</sub>O below unity, which is its value in the standard state. How would you measure the activity water saturated with salt?

#### 3. The fuel cell is founded on the following reaction



$$\text{where } \mu_{H_2O} = \mu_{H_2O}^{\circ} + RT \ln p_{H_2O}, \quad (3.2)$$

$$\mu_{H_2} = \mu_{H_2}^{\circ} + RT \ln p_{H_2}, \text{ and}$$

$$\mu_{O_2} = \mu_{O_2}^{\circ} + RT \ln p_{O_2}$$

The work available from Eq. (3.1) is given by

Available work from the reaction between oxygen and hydrogen, per mole of H<sub>2</sub>O is given by

$$\Delta G_{H_2O} = \mu_{H_2O} - \mu_{H_2} - 0.5\mu_{O_2} = \left(\mu_{H_2O}^{\circ} - \mu_{H_2}^{\circ} - \frac{1}{2}\mu_{O_2}^{\circ}\right) + RT \ln p_{H_2O} - RT \ln p_{H_2} - \frac{1}{2}RT \ln p_{O_2} \quad (3.3)$$

Now,

$$\Delta G_{H_2O}^{\circ} = \left(\mu_{H_2O}^{\circ} - \mu_{H_2}^{\circ} - \frac{1}{2}\mu_{O_2}^{\circ}\right) \quad (3.4)$$

The quantities on the right are in their standard state, that is as a gas at 1 atm pressure. The free energy of formation of water vapor in the standard state is given in JANAF tables

<https://janaf.nist.gov/tables/H-064.html>

(the standard free energies of formation for many compounds are found in <https://janaf.nist.gov>)

The data for water vapor from JANAF

Water (H<sub>2</sub>O)H<sub>2</sub>O<sub>1</sub>(g)Enthalpy Reference Temperature =  $T_r = 298.15$  KStandard State Pressure =  $p^\circ = 0.1$  MPa

| $T/K$  | $J \cdot K^{-1} \cdot mol^{-1}$ |           |                               |                    | $kJ \cdot mol^{-1}$ |                    |            |
|--------|---------------------------------|-----------|-------------------------------|--------------------|---------------------|--------------------|------------|
|        | $C_p^\circ$                     | $S^\circ$ | $-[G^\circ - H^\circ(T_r)]/T$ | $H - H^\circ(T_r)$ | $\Delta_f H^\circ$  | $\Delta_f G^\circ$ | $\log K_f$ |
| 0      | 0.                              | 0.        | INFINITE                      | -9.904             | -238.921            | <b>-238.921</b>    | INFINITE   |
| 100    | 33.299                          | 152.388   | 218.534                       | -6.615             | -240.083            | <b>-236.584</b>    | 123.579    |
| 200    | 33.349                          | 175.485   | 191.896                       | -3.282             | -240.900            | <b>-232.766</b>    | 60.792     |
| 298.15 | 33.590                          | 188.834   | 188.834                       | 0.                 | -241.826            | <b>-228.582</b>    | 40.047     |
| 300    | 33.596                          | 189.042   | 188.835                       | 0.062              | -241.844            | <b>-228.500</b>    | 39.785     |
| 400    | 34.262                          | 198.788   | 190.159                       | 3.452              | -242.846            | <b>-223.901</b>    | 29.238     |
| 500    | 35.226                          | 206.534   | 192.685                       | 6.925              | -243.826            | <b>-219.051</b>    | 22.884     |
| 600    | 36.325                          | 213.052   | 195.550                       | 10.501             | -244.758            | <b>-214.007</b>    | 18.631     |
| 700    | 37.495                          | 218.739   | 198.465                       | 14.192             | -245.632            | <b>-208.812</b>    | 15.582     |
| 800    | 38.721                          | 223.825   | 201.322                       | 18.002             | -246.443            | <b>-203.496</b>    | 13.287     |
| 900    | 39.987                          | 228.459   | 204.084                       | 21.938             | -247.185            | <b>-198.083</b>    | 11.496     |
| 1000   | 41.268                          | 232.738   | 206.738                       | 26.000             | -247.857            | <b>-192.590</b>    | 10.060     |
| 1100   | 42.536                          | 236.731   | 209.285                       | 30.191             | -248.460            | <b>-187.033</b>    | 8.881      |
| 1200   | 43.768                          | 240.485   | 211.730                       | 34.506             | -248.997            | <b>-181.425</b>    | 7.897      |

We are interested in the Gibbs Free Energy of formation of water vapor given above as a function of temperature.

•Note that the free energies are negative quantities which means that the right hand side of Eq. (3.1) is lower than the left hand side, that is, energy is released by the reaction to the environment.

•These values refer to the reaction carried out with hydrogen and oxygen at one atm., i.e. the standard state.

**The Energy Available at non-standard pressure of oxygen and hydrogen is given by,**

$$\Delta G_{H_2O} = \Delta G_{H_2O}^\circ + RT \ln p_{H_2O} - RT \ln p_{H_2} - \frac{1}{2} RT \ln p_{O_2} \quad (3.5)$$

In the fuel cell hydrogen is injected on one side of the membrane (the electrolyte), and oxygen on the other side. The oxygen diffuses through the electrolyte and reacts with the hydrogen to produce water vapor. Thus one has the mixture of water vapor and hydrogen on the fuel side and oxygen on the other side. The total vapor pressure is 1 atm on both sides.

Now consider how the work available, that is  $\Delta G_{H_2O}$  is influenced by the vapor pressure of the three species.

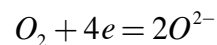
Notes:

- meaning that the reaction releases energy to the environment. Let us say that the fuel cell is operated at 1000 K, then from the above table  $\Delta G_{H_2O}^{\circ}(1000\text{ K}) = -193\text{ kJmol}^{-1}$ .
- Lower  $p_{H_2O}$  makes the LHS of Eq. (3.5) more negative so that more work is available. Typical number is  $p_{H_2O} = 0.05$ .
- The negative signs in front of oxygen and hydrogen terms means that their vapor pressures should be as high as possible so that  $\Delta G_{H_2O}^{\circ}$  is as negative a value as possible.
- Typically air is used to supply oxygen so that  $p_{O_2} \approx 0.2$
- Typically the sum of the pressure on the fuel side, which is the sum of vapor pressures of H<sub>2</sub>O and H<sub>2</sub> is equal to one. Since  $p_{H_2O}$  is assumed to be 0.05 atm. we have that  $p_{H_2} \approx 0.95$  atm.

**You are now asked to calculate how much energy is released per mole of hydrogen fuel?**

**I would like you to think about the following as much as you can.**

The energy released from the above analysis is converted into electrical work by devising the following reaction to occur



where “e” represents an electron, more specifically the charge on one electron. The right hand side is an oxygen ion with a charge of two minus (that is the charge of two electrons). Note how the equation above is balanced in mass and in charge.

The electrical work is done by having the electrons flow through the electrical load. Let us say that the voltage across the fuel cell is  $V_o$  volts. Then the work done per mole of hydrogen fuel is given by

$V_o$  \*(charge flowing per mole of hydrogen fuel) must be equal to  $\Delta G_{H_2O}$  as calculated above.

Try to obtain a value for  $V_o$ .