

## Lecture 07

### Free energy and chemical thermodynamics

Enthalpy  $H = U + PV$  is the energy you need to create a system out of nothing and put it into environment at pressure  $P$ .

Let us introduce new function,  $F = U - TS$  -- Helmholtz free energy

It has following important properties

1)  $dF = dU - TdS - SdT$  and using thermod. identity  $dU = TdS - PdV$

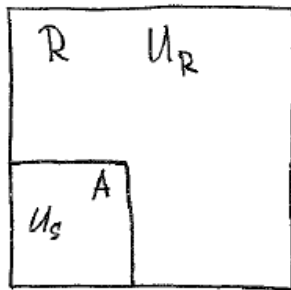
$$dF = -PdV - SdT$$

If temperature is constant

$$dF = -PdV = -dW_s \leftarrow \text{in reversible process}$$

This means that total work performed **on a system** in reversible isothermal process is equal to an increase in the Helmholtz free energy.

2) The Helmholtz free energy will be a minimum for a system  $A$  in thermal contact with a reservoir  $R$  if the volume of the system is constant.



If temperature is constant then  $dF = dU - TdS - SdT = dU - TdS$  if we transfer energy  $dU$  from  $R$  to  $A$  then the free energy change as

$$dF_s = dU_s - TdS_s \quad dS_s - \text{change of the entropy of the system}$$

$$\text{On the other hand} \quad \frac{1}{T} = \left( \frac{\partial S_s}{\partial U_s} \right)_v \quad \text{so}$$

$$dU_s = TdS_s \text{ and therefore}$$

$$dF_s = 0 - \text{which correspond to the position of extremum.}$$

It can be farther shown that it corresponds to minimum of  $F_s$

Many energy transfer processes take place at constant pressure, particularly those processes that take place in system open to the atmosphere. A process at constant pressure is said to be isobaric process.

If we have a process at constant temperature and constant pressure it is convenient to introduce new function

$G = U + PV - TS$  –Gibbs free energy. The we may consider the change in the Gibbs Free energy

$$dG = dU + d(PV) - d(TS) = dU + d(PV) - d(Q) = -dW_S = dW_{EXT} ,$$

where the  $dW_S$  is the work done by system excluding a work spent in expansion or contraction of a system volume.  $dW_{EXT}$  is a work done on system excluding a work spent in expansion or contraction of a system volume. We have used the following splitting of the work in the first law of thermodynamics.

$$dU = dQ - dW_{ST} = dQ - dW_S - PdV$$

The effective (useful) work performed in a reversible process at constant temperature and pressure is equal to the change in the Gibbs free energy of the system.

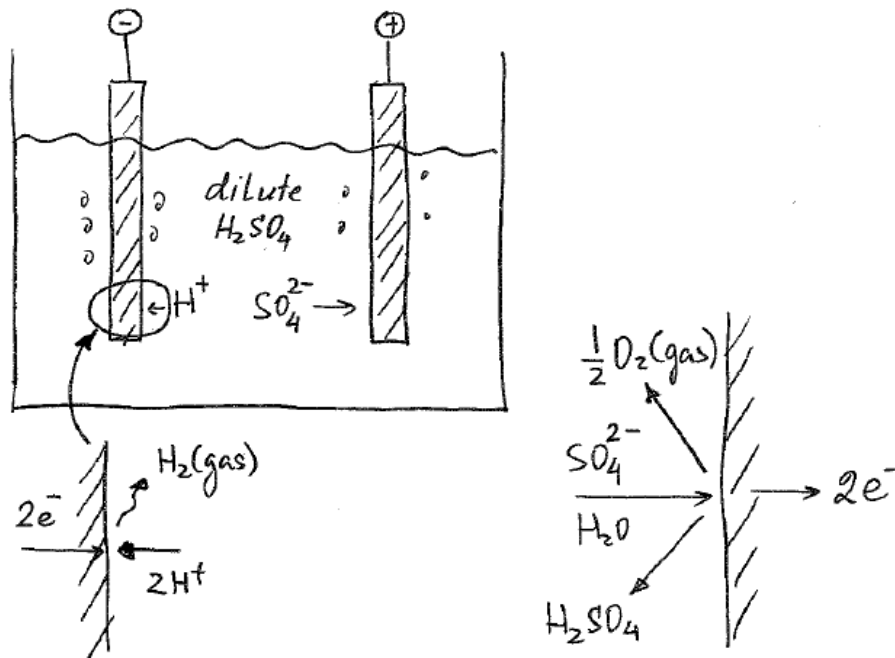
$U, F, H, G$  are collectively called thermodynamic potentials.

$$dG = dU + PdV - TdS \quad (T, P_{const})$$

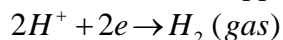
$$dG = dH - TdS$$

### Example

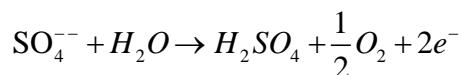
**Electrolysis** is a process that both isothermal and isobaric



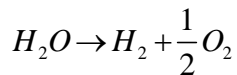
When current moves through the cell the  $H^+$  moves to the negative electrode and  $SO_4^{2-}$  ions move to the opposite electrode at  $(-)$  electrode reaction is



at  $\oplus$  electrode reaction is



The sum of above reactions is



When carried out slowly in a vessel open to atmosphere, the process is at constant pressure and constant temperature. A negligible part of the electrical input power goes into resistance heating of electrolyte.

The effective work required to decompose 1 mole of water is related to the molar Gibbs free energy of the reactions:

$$W_{ext} = \Delta G = \Delta_f G(H_2) + \frac{1}{2} \Delta_f G(O_2) - \Delta_f G(H_2O)$$

In electrolysis this work is performed by a current  $I$  that flows under an external voltage  $V_0$ . If  $t$ -time needed to decompose 1 mole of water than

$Q = It$  -  $Q$  - total charge passed through the cell

$W = QV_0$  - total electrical work.

2e are involved in decomposition of 1 water molecule  $\Rightarrow$

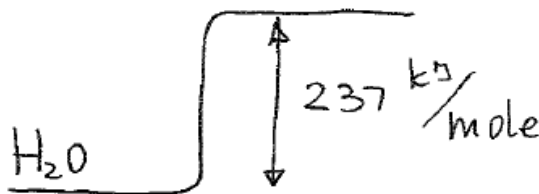
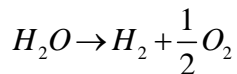
$$Q = -2N_A e = -2 \times 6.02 \times 10^{23} \times 1.6 \times 10^{-19} = -1.93 \times 10^{-5} \text{ coulomb}$$

$$W_{ext} = QV_0 = \Delta G$$

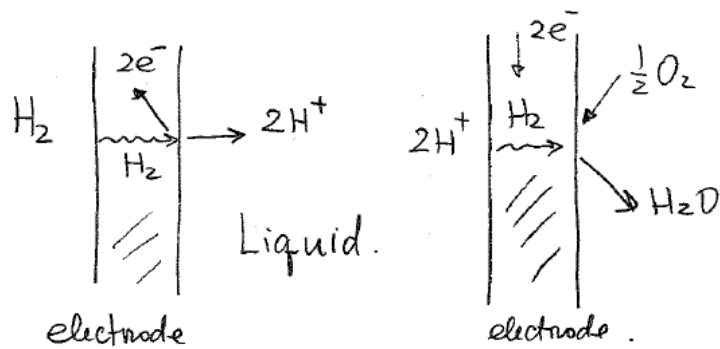
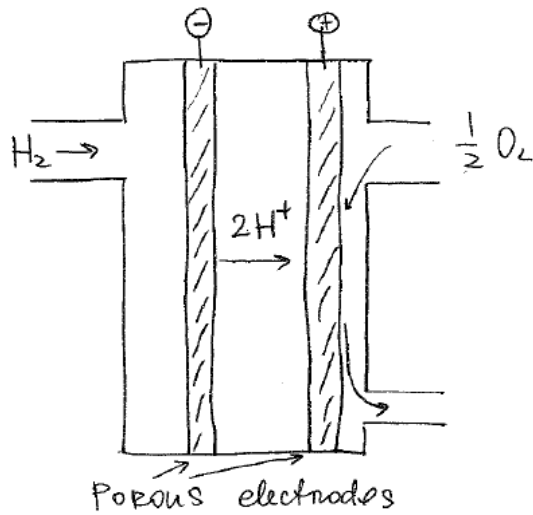
The above equation determines condition for electrolysis

$$V_0 = \frac{\Delta G}{Q} = -\frac{\Delta G}{2N_A e} = 1.23V$$

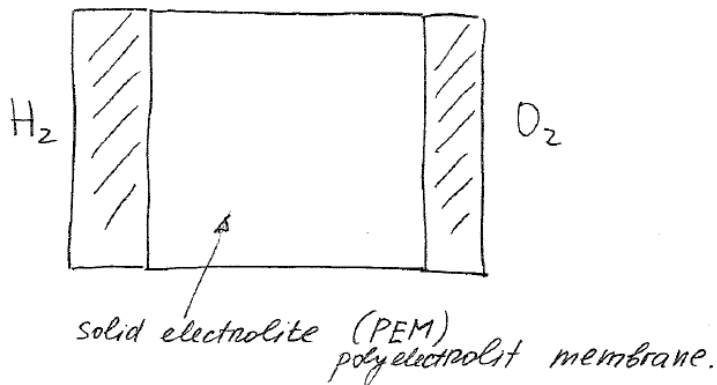
A voltage large than  $V_0$  must be applied for current to flow, because  $V_0$  alone barely reduces to zero the potential barrier in reaction



If  $V < V_0$  the reaction will proceed from right to left provided gaseous  $O_2$  is available at the negative electrode and gaseous  $H_2$  is available. Design of *hydrogen-oxygen* fuel all allows getting some voltage and current following the external circuit.

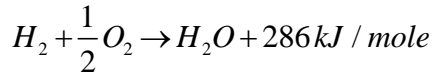


Another possible arrangement



Another possible solid electrode is  $ZrO_2$  – negative oxygen ion  $O^{2-}$  are moving charge in this solid electrolyte.

To get  $V_0$  we used table value for  $\Delta G = -237 \text{ kJ / mole}$ . Let's find out how we get this number in the first place.



286 kJ is heat you get out of burning 1 mole of H<sub>2</sub>.

$\Delta H(H_2O) = -286 \text{ kJ}$  (Look at table on page 405)

-286 kJ – enthalpy of formation from elements in their stable standard state at T = 300k and P = 1 atm.

If we now run the reaction in reverse  $H_2O \rightarrow H_2 + \frac{1}{2} O_2$  we need to put 286 kJ of energy in the system in one way or other.

When we convert H<sub>2</sub>O into H<sub>2</sub> and O<sub>2</sub> we increase the entropy of the system,

$$\Delta S = \frac{1}{2} S_{O_2} + S_{H_2} - S_{H_2O} = \frac{1}{2} (205 \text{ J / K}) + 131 \text{ J / K} - 70 \text{ J / K} = 163 \text{ J / K}$$

But because our system is in thermal equilibrium at temperature T we may get the part of the energy needed for entropy change from environment for free in the form of heat.

$$\Delta Q = T \Delta S = 298 \text{ K} \times 163 \text{ J / K}$$

$$\Delta G = \Delta H - T \Delta S = 286 \text{ kJ} - (298 \text{ K}) \cdot (163 \text{ J / K}) = 237 \text{ J}$$