

02A Thermodynamics of Energy Conversion:

Gibbs Free Energy and the Chemical Potential

Objective

Topic I: The Thermodynamics of Energy Transformation

The transformation of chemical energy into electrical energy.

Chemical Energy: Change in the Gibbs Free Energy of the System. Must be negative to do work on the environment. It is expressed in units of kJ mol^{-1} .

Electrical Energy: $\text{Watts} \cdot \text{seconds} = \text{volts} \cdot \text{amps} \cdot \text{seconds}$. $\text{Amps} \cdot \text{seconds} \rightarrow \text{coulombs}$. $\text{Coulombs} \cdot \text{volts} \rightarrow \text{J}$. Remember that a Watt is one J s^{-1} . $\text{Watt} = \text{current} \cdot \text{volts}$.

The change in the Gibbs Free Energy is the maximum amount of electrical work that can be available from a cell.

The Species: the critical species in the battery function.

Gibbs Free Energy is a system variable. That must be reduced to the chemical potential of the critical species that is the basis for the battery or the fuel cell.

Topic II: Solid Oxide Fuel Cell (SOFC)

What is the critical species (oxygen ion)?

What are the properties of the electrolyte?

What are the properties of the anode and the cathode?

What are the performance measures of the SOFC?

Topic III: Lithium-Ion Battery

What is the critical species (Lithium ion)?

What are the properties of the electrolyte?

What are the properties of the anode and the cathode?

Performance of lithium-ion batteries?

Topic I: The Thermodynamics of Energy Transformation

Gibbs Free Energy

Gibbs Free Energy is a "system level" phenomenon. When considered as the difference between two states of matter, such that the overall composition remains unchanged, then

If $G_{II} - G_I < 0$ then the magnitude of the difference is equal to the work that the system does on the surroundings. This is an "exothermic" reaction, i.e. heat is released, or work is done towards the environment.

If $G_{II} - G_I > 0$ then the magnitude of the difference is equal to the work that the environment has to do to move the system from I to II. In this instance the reaction is "endothermic".

If $G_{II} = G_I$ then the two states are in equilibrium with each other.

Gibbs and the Chemical Potential

The Gibbs Free energy of a system is the sum of the chemical potentials of all its constituents. That is

$$G_{system} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + \dots \quad (1)$$

Chemical Potential and the Standard State

The standard state of a species is a reference condition. For example the standard state of $O_2(g)$, oxygen is the species in the gaseous state. The standard state of

- standard state [$O_2(g)$] is pure oxygen gas at one atm pressure and a given temperature.
- Standard state of Li (solid) is pure Li at a specific temperature and pressure.

Note the emphasis on "pure". For air which is 20% oxygen is not a standard state.

The General Chemical Potential

The general chemical potential of a species is given by

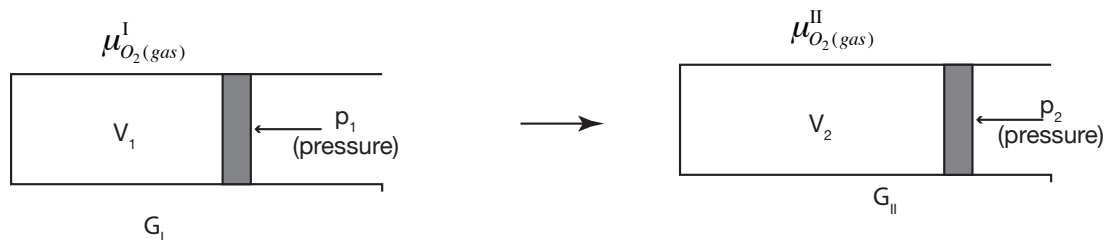
$$\mu_{specie} = \mu_{specie}^o + RT \ln [a_{specie}] \quad (2)$$

where μ_{specie}^o is the chemical potential in the standard state, and a_{specie} is the "activity" of the species in an away-from-standard state.

• The activity of a condensed phase where the specie is in pure form the activity is equal to one. For example for pure lithium metal the activity = unity, because for a pure lithium metal $\mu_{Li} = \mu_{Li}^o$ since $\ln(1) = 0$.

• The activity of a gas phase (ideal gas) is equal to its partial pressure in the system. For example the activity of oxygen in ambient atmosphere = 0.2, while the activity of nitrogen = 0.8. Trace gases, like He would have very low activities.

Show that the activity of a gas is equal to its partial pressure



$$\mu_{p_{O_2}}^{(2)} - \mu_{p_{O_2}}^{(1)} = - \int_{V_1}^{V_2} p dV, \text{ minus sign since the system does work on the environment.}$$

$$PV = RT$$

$$\mu_{p_{O_2}}^{(2)} - \mu_{p_{O_2}}^{(1)} = - \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_1}{V_2} = RT \ln \frac{p_2}{p_1} \quad (3)$$

Note that the right-hand side is negative since the system is doing work on the environment.

Let us consider the event as the difference in the Free Energy,

$$\Delta G_{II-I} = n\mu_{O_2}^{II} - n\mu_{O_2}^I$$

We can drop n since it does not affect the results.. it is simply a multiplier.

Substituting from Eq. (2)

$$\begin{aligned} \frac{\Delta G_{II-I}}{n} &= [\mu_{O_2}^o + RT \ln(a_{O_2}^{II})] - [\mu_{O_2}^o + RT \ln(a_{O_2}^I)] \\ &= RT \ln \frac{a_{O_2}^{II}}{a_{O_2}^I} \end{aligned} \quad (4)$$

Comparing Eqns (3) and (2) we note that

$$a_{O_2} = p_{O_2} \quad \text{an important general result} \quad (5)$$

Let us Discuss the Principal of a Solid Oxide Fuel Cell (SOFC)

The thermodynamics of an SOFC is that oxygen is on one side and hydrogen on the other side. Oxygen diffuses as ions through the electrolyte, which reacts with the hydrogen to release chemical energy as electrons that are transported through the environment to do electrical work. The reaction is that the oxygen in air ionizes to capture electrons (meaning that O_2 becomes $2O^{2-}$), and released electrons at the hydrogen electrode thereby completing the electrical current (meaning that $2O^{2-}$ converts back to O_2)

$$\Delta G = RT \ln \frac{a_{O_2}^{air}}{a_{O_2}^{hydrogen}} = RT \ln \frac{p_{O_2}^{air}}{p_{O_2}^{hydrogen}} \quad (6)$$

Now, we must calculate the activity of oxygen at the hydrogen electrode. We shall address this question under Topic 3 (REDOX Reactions)