

Energetics and Equilibria

Revision

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12 May, 2018

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1 Laws of Thermodynamics

1.1 2nd Law

What's the universal/general cause/reason for spontaneous processes? → 2nd Law:

In a spontaneous process the **entropy** of the Universe increases.

1.1.1 Molecular Definition of Entropy

Measure of randomness using the number of ways to arrange particles into different states.

$$S = k \ln W \quad (1)$$

where

$$W = \frac{(\sum n_i)!}{\prod (n_i!)} \quad (2)$$

k is Boltzmann's constant.

The distribution to maximise W (most probable by 2nd Law) is the Boltzmann Distribution:

$$n_i = n_0 \exp\{(-\varepsilon_i/kT)\} \quad (3)$$

where $\varepsilon_0 = 0$, ε_i is the energy of state i .

1.1.2 Classical Definition of Entropy

$$dS = \frac{\delta q_{\text{rev}}}{T} \quad (4)$$

dS : differential of S since S is a state function; δq_{rev} is NOT differential since heat is not a state function.

1.2 Universe = System + Surroundings

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad (5)$$

1.2.1 Surrounding is LARGE

Therefore, two assumptions for the surroundings:

1. T_{surr} does not change
2. Heat exchanged with the system can be considered as reversible

Then:

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} \quad (6)$$

also $q_{\text{surr}} = -q_{\text{sys}}$, assume $T_{\text{surr}} = T_{\text{sys}}$, then

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T_{\text{sys}}} \quad (7)$$

$\Delta S_{\text{univ}} = 0$ at equilibrium.

1.3 1st Law

1st Law states the conservation of different forms of energy.

$$\Delta U = q + w \quad (8)$$

simply means the change in internal energy U of the system is the sum of heat transfer into the system q and the work done *on* the system w .

If change sign convention, take the work done *by* the system, w' , 1st Law is

$$\Delta U = q - w' \quad (9)$$

Notice the difference between State Functions (same state, same value) and Path Functions (paths dependent).

2 Gas Expansion

2.1 Ideal Gas Law

Simply

$$pV = nRT \quad (10)$$

2.2 Gas as a Thermal System in Expansion

The element work done by gas when expanding against external pressure p_{ext} is

$$\delta w' = p_{\text{ext}} dV \quad (11)$$

2.2.1 Constant External Pressure Expansion

Using damn simple integration, work done by the gas is

$$w' = p_{\text{ext}}(V_2 - V_1) \quad (12)$$

2.2.2 Reversible Process, Maximum Work

A reversible process is one in which the work is a maximum or the work done in a reversible process is maximum.

Reversible Processes:

- Infinitely slow
- At equilibrium
- Do maximum work

Irreversible Processes (Spontaneous):

- Go at finite rate
- Not at equilibrium
- Do less than the maximum work

2.2.3 Reversible Isothermal Expansion, Ideal Gas

Reversible, $p_{\text{ext}} = p_{\text{int}}$

$$w' = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1} \quad (13)$$

Isothermal, T is a constant. Also, $\Delta U = 0$.

2.2.4 *Work and Heat*

Relate these using 1st Law.

2.2.5 *Entropy and Reversible Heat*

For the reversible isothermal, $q = w'$, then the change in entropy of the gas is

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad (14)$$

Clearly, the entropy increases with volume.

3 **U, H, C, S**

3.1 Differential Forms of Internal Energy

$$dU = \delta q - p dV \quad (15)$$

under circumstances where pV work only.

3.2 Constant VOLUME - Internal Energy

When the volume of the system is constant,

$$dU = \delta q_{\text{const. vol}} \quad (16)$$

3.2.1 *Introducing Heat Capacity*

The heat capacity is the coefficient of proportionality of in the relationship $q \propto \Delta T$. Taking differentials, we have

$$\delta q = c dT \quad (17)$$

Concerning about the amount of substance, the molar heat capacity C_m arises in

$$q = nC_m \Delta T \quad (18)$$

3.2.2 *Using Heat Capacity*

By the constant volume assumption, $\Delta U = nC_{V,m} \Delta T$, taking differentials, we have

$$dU_m = C_{V,m} dT \quad (19)$$

where dU_m is the change in the *molar* internal energy.

Thus we have:

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V \quad (20)$$

3.3 Constant PRESSURE - Enthalpy

3.3.1 *Introducing Enthalpy*

Enthalpy is the Legendre Conjugate of U about V , defined as

$$H = U + pV \quad (21)$$

then taking differential, we have

$$dH = \delta q + Vdp \quad (22)$$

By the same argument, under constant pressure

$$dH = \delta q_{\text{const. press.}} \quad (23)$$

This shows enthalpy is convenient when studying constant pressure processes.

3.3.2 *Using Heat Capacity*

By the similar argument

$$C_{p,m} = \left(\frac{\partial H_m}{\partial T} \right)_p \quad (24)$$

3.3.3 *Enthalpy as a Function of Temperature*

Easy to see that

$$dH_m = C_{p,m}dT \quad (25)$$

therefore

$$H_m(T_2) = H_m(T_1) + \int_{T_1}^{T_2} C_{p,m}dT \quad (26)$$

If constant $C_{p,m}$, we have

$$H_m(T_2) = H_m(T_1) + C_{p,m}(T_2 - T_1) \quad (27)$$

3.4 Heat Capacities

Heat Capacities do vary with temperature T , but not too strongly. Usually

$$C(T) = a + bT + \frac{c}{T^2} \quad (28)$$

This can be tabulated and C for different temperatures can be found.

3.5 Absolute Entropies

Using the constant pressure argument

$$dS = \frac{dH}{T} = \frac{C_{p,m}(T)}{T}dT \quad (29)$$

But in practical situation, we need to consider the entropy change while the phase changes since at the point of phase change, the temperature does not vary when heat transfer is in process (i.e. $C_{p,m}$ is infinite). Also, by noticing the entropy at absolute zero temperature is zero, we have

$$S_m(T^*) = \int_0^{T^*} \frac{C_{p,m}(T)}{T}dT + \sum_{\text{phase change}} \frac{\Delta H_{m,pc}}{T_{pc}} \quad (30)$$

Most of times, we can assume $C_{p,m}$ in the concerned range is constant and there's no phase change. Then by integration

$$S_m(T_2) = S_m(T_1) + C_{p,m} \ln \frac{T_2}{T_1} \quad (31)$$

4 Gibbs Energy

Gibbs energy is a convenient way of using the 2nd Law. It is easier to use Gibbs energy to determine the spontaneity of processes.

As always, Gibbs Energy is another Legendre conjugate. It is the conjugate of enthalpy H about S , defined as

$$G = H - TS \quad (32)$$

4.1 Gibbs Energy and Universal Entropy

The three assumptions of the following arguments are

- Constant temperature
- Temperature of the system is the same as that of the surroundings
- Constant pressure

Then, by taking differentials

$$dG = dH - TdS - SdT \quad (33)$$

Note that the temperature is constant, so

$$-\frac{dG_{\text{sys}}}{T_{\text{sys}}} = -\frac{dH_{\text{sys}}}{T_{\text{sys}}} + dS_{\text{sys}} \quad (34)$$

Also we notice that

$$dS_{\text{univ}} = -\frac{dH_{\text{sys}}}{T_{\text{sys}}} + dS_{\text{sys}} \quad (35)$$

showing that

$$-\frac{dG_{\text{sys}}}{T_{\text{sys}}} = dS_{\text{univ}} \quad (36)$$

Then we have

$$dS_{\text{univ}} > 0 \Leftrightarrow dG < 0 \quad (37)$$

for spontaneous process. Both are zero at equilibrium (i.e. G reaches minimum).

Then it is easy to derive the famous equation

$$\Delta G = \Delta H - T\Delta S \quad (38)$$

4.2 Variation of Gibbs Energy with Pressure and Temperature

4.2.1 Master Equations

This is well-known

$$dU = TdS - pdV \quad (39)$$

By definitions of H and G we easily derive

$$dH = TdS + Vdp \quad (40)$$

$$dG = Vdp - SdT \quad (41)$$

4.2.2 Variation of G with p at constant T

At constant T , simply

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (42)$$

For ideal gas, by simple integration, we have

$$G(p_2) = G(p_1) + nRT \ln \frac{p_2}{p_1} \quad (43)$$

By taking the molar term and assuming the initial value is at standard pressure $p^\ominus = 1$ bar, then

$$G_m(p) = G_m^\ominus + RT \ln \frac{p}{p^\ominus} \quad (44)$$

By $p_2/p_1 = V_1/V_2$, we have (this is not rigorous since we changed the independent variable, so I shall call the function G')

$$G'_m(V_2) = G'_m(V_1) = nRT \ln \frac{V_1}{V_2} \quad (45)$$

4.3 Variation of G with T at constant p

At constant p , simply

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (46)$$

It is easy to verify that

$$\frac{d}{dT} \left(\frac{G}{T}\right) = -\frac{H}{T^2} \quad (47)$$

using $dG/dT = -S$ and $G = H - TS$. This is called the *Gibbs-Helmholtz Equation*.

4.4 Gibbs Energy of Mixtures

4.4.1 Partial Pressure

Partial pressure of gas i in a mixture of gases is defined as

$$p_i = x_i p_{\text{tot}} \quad (48)$$

where

$$x_i = \frac{n_i}{n_{\text{tot}}} = \frac{n_i}{\sum_i n_i} \quad (49)$$

4.4.2 Gibbs Energy of Components in a Mixture

Easy to see

$$G_{m,i}(p_i) = G_{m,i}^\ominus + RT \ln \frac{p_i}{p^\ominus} \quad (50)$$

4.4.3 Gibbs Energy of Mixture

It is easy to say it is

$$G = \sum_i n_i G_{m,i}(p_i) \quad (51)$$

but this is not general enough.

4.5 Introducing the Chemical Potential

Chemical potential μ_i for each species i in a mixture gives us the Gibbs energy of the whole mixture simply by

$$G = \sum_i n_i \mu_i \quad (52)$$

4.5.1 Chemical Potential of a Gas

Similar to Gibbs energy, for a gas i

$$\mu_i(p_i) = \mu_i^\ominus + RT \ln \frac{p_i}{p^\ominus} \quad (53)$$

this boils down to Gibbs energy of the component if the gas is ideal. Also, we can say that μ_i' can be expressed as a “function” in V .

4.5.2 Chemical Potential of a Solution

Similar idea

$$\mu_i(c_i) = \mu_i^\ominus + RT \ln \frac{c_i}{c^\ominus} \quad (54)$$

where c_i is the concentration of solute i and $c^\ominus = 1 \text{ mol dm}^{-3}$ is the standard concentration. This assumes that the solution is ideal (in fact, this is rare in practice but we just use this as approximation).

4.5.3 Chemical Potential of Solid or Liquid

Always in standard state, the chemical potential is μ_i^\ominus .

5 Chemical Changes

5.1 About Δ_r

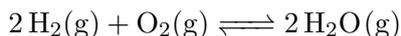
The Δ_r symbol is related with change in different physical quantities when *one mole of reaction* takes places at the specified and constant composition. When define $\Delta_r H$ as the change in enthalpy, $\Delta_r G$ and $\Delta_r S$ as the change in Gibbs energy and entropy, respectively.

5.2 Standard States and Standard Changes

The standard state of a substance is the *pure* form at a pressure of *one bar* and at the *specified temperature*.

The standard state is usually denoted using the underground symbol ($^\ominus$).

EXAMPLE. In reaction



$\Delta_r H^\ominus$ is the enthalpy change when two moles of H_2 reacts with one mole of O_2 to give two moles of H_2O , all species being in their standard states. Notice that this implies pure substances, i.e. no mixing.

5.2.1 Enthalpies of Formation

The standard enthalpy of formation of a compound $\Delta_f H^\ominus$ is the standard enthalpy change for a reaction in which one mole of the compound is formed from its constituent elements at a pressure of 1 bar. This is often tabulated.

Generally, for reaction



by Hess's Law, we have

$$\Delta_r H^\ominus = \sum_j [\lambda_j \Delta_f H^\ominus(\text{P}_j)] - \sum_i [\nu_i \Delta_f H^\ominus(\text{R}_i)] \quad (56)$$

5.2.2 Standard Entropy and Gibbs Energy Change for Reactions

For the same reaction, similarly, the standard entropy change is

$$\Delta_r S^\ominus = \sum_j [\lambda_j S_m^\ominus(\text{P}_j)] - \sum_i [\nu_i S_m^\ominus(\text{R}_i)] \quad (57)$$

Then, clearly

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus \quad (58)$$

Sometimes, $\Delta_f G^\ominus$ is tabulated.

5.3 Variation of $\Delta_r H^\ominus$ with Temperature

Recall from $dH_m/dT = C_{p,m}$, we can see

$$\frac{d\Delta_r H^\ominus}{dT} = \Delta_r C_p^\ominus \quad (59)$$

under standard state.

For the same general reaction, we define

$$\Delta_r C_p^\ominus = \sum_j [\lambda_j C_{p,m}^\ominus(\text{P}_j)] - \sum_i [\nu_i C_{p,m}^\ominus(\text{R}_i)] \quad (60)$$

For constant $C_{p,m}^\ominus$ with respect to each compound, we derive

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \Delta_r C_p^\ominus [T_2 - T_1] \quad (61)$$

for different temperatures T_1 and T_2

5.4 Variation of $\Delta_r S^\ominus$ with Temperature

For the same argument

$$\Delta_r S^\ominus(T_2) = \Delta_r S^\ominus(T_1) + \Delta_r C_p^\ominus \ln \frac{T_2}{T_1} \quad (62)$$

6 Equilibrium

6.1 Equilibrium Constants

For general reversible reaction



The equilibrium constant in terms of partial pressure is defined as

$$K_p = \frac{\prod_j \left(\frac{p(\text{P}_j)}{p^\ominus} \right)^{\lambda_j}}{\prod_i \left(\frac{p(\text{R}_i)}{p^\ominus} \right)^{\nu_i}} \quad (64)$$

Note that solid or liquid do not take part in this equation.

The equilibrium constant in terms of concentrations is defined as

$$K_c = \frac{\prod_j \left(\frac{c(\text{P}_j)}{c^\ominus} \right)^{\lambda_j}}{\prod_i \left(\frac{c(\text{R}_i)}{c^\ominus} \right)^{\nu_i}} \quad (65)$$

6.2 Condition for Chemical Equilibrium

Recall from the chemical potentials, for the general reaction above, we have

$$\Delta_r G = \sum_j \lambda_j \mu(\text{P}_j) - \sum_i \nu_i \mu(\text{R}_i) \quad (66)$$

Clearly, at equilibrium, $\Delta_r G = 0$

6.3 Relations between $\Delta_r G^\ominus$ with Equilibrium Constants

Still, for the same general reaction

$$\begin{aligned} \Delta_r G &= \sum_j \lambda_j \mu(\text{P}_j) - \sum_i \nu_i \mu(\text{R}_i) \\ &= \sum_j \lambda_j \left(\mu^\ominus(\text{P}_j) + RT \ln \frac{p(\text{P}_j)}{p^\ominus} \right) - \sum_i \nu_i \left(\mu^\ominus(\text{R}_i) + RT \ln \frac{p(\text{R}_i)}{p^\ominus} \right) \\ &= \left(\sum_j \lambda_j \mu^\ominus(\text{P}_j) - \sum_i \nu_i \mu^\ominus(\text{R}_i) \right) + RT \ln \left(\frac{\prod_j \left(\frac{p(\text{P}_j)}{p^\ominus} \right)^{\lambda_j}}{\prod_i \left(\frac{p(\text{R}_i)}{p^\ominus} \right)^{\nu_i}} \right) \\ &= \Delta_r G^\ominus + RT \ln \left(\frac{\prod_j \left(\frac{p(\text{P}_j)}{p^\ominus} \right)^{\lambda_j}}{\prod_i \left(\frac{p(\text{R}_i)}{p^\ominus} \right)^{\nu_i}} \right) \end{aligned}$$

At equilibrium, $\Delta_r G = 0$, also put in K_p , we have

$$\Delta_r G^\ominus = -RT \ln K_p \quad (67)$$

By the same argument, we can also have

$$\Delta_r G^\ominus = -RT \ln K_c \quad (68)$$

6.4 Interpreting $\Delta_r G^\ominus = -RT \ln K$

It can be rewritten as

$$K = \exp\left\{\frac{-\Delta_r G^\ominus}{RT}\right\} \quad (69)$$

When $\Delta_r G^\ominus > 0$, the reaction is not favourable, K is much smaller than 1, meaning that the reaction goes towards the reactants. Similar for other cases.

6.5 Influencing Equilibrium

6.5.1 Le Chatelier's Principle

Le Chatelier's Principle states that

When a system in equilibrium is subjected to a change, the composition of the equilibrium mixture will alter in such a way as to counteract the change.

6.5.2 Effect of Concentration

Use Le Chatelier's Principle.

6.5.3 Effect of Temperature

Simply by $\Delta_r G^\ominus = -RT \ln K$ and $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$, we have

$$\ln K = \frac{-\Delta_r H^\ominus}{R} \frac{1}{T} + \frac{\Delta_r S^\ominus}{R} \quad (70)$$

Recall the Gibbs-Helmholtz equation and with the relationship between $\Delta_r G^\ominus$ with K , we have the *van't Hoff isochore*

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2} \quad (71)$$

this integrate to give the same answer

$$\ln K = \frac{-\Delta_r H^\ominus}{R} \frac{1}{T} + \text{const.} \quad (72)$$

6.5.4 Effect of Pressure

EXAMPLE. Think about a reaction



Let n_0 be the initial amount of A_2 and α be the fraction of A_2 molecules which have dissociated. Then after dissociation, the amount of A_2 is $(1 - \alpha)n_0$ and the amount of A is $2\alpha n_0$. The total pressure is p_{tot} . Then

$$p(\text{A}_2) = \frac{1 - \alpha}{1 + \alpha} p_{\text{tot}}$$
$$p(\text{A}) = \frac{2\alpha}{1 + \alpha} p_{\text{tot}}$$

Then

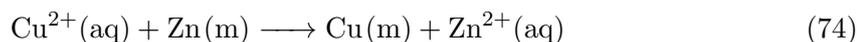
$$K_p = \frac{4\alpha^2}{1 - \alpha^2} \frac{p_{\text{tot}}}{p^\ominus}$$

But we know that when p_{tot} is varied, K_p does not change. It must be α that changes. If we approximate that $\alpha \ll 1$ then

$$\alpha = \sqrt{\frac{K_p p^\ominus}{4p_{\text{tot}}}} \quad (73)$$

7 Electrochemistry

We will use the following reaction as the major example throughout this section

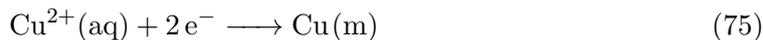


7.1 Cell Conventions

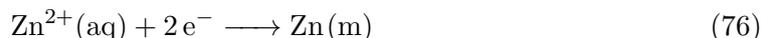
Cell conventions is for convenience in discussion.

7.1.1 Half-Cell Reactions and Couples

It is reasonable to think the whole reaction in terms of two half cells. In LHS half cell, the reaction is



and in the other, the RHS cell, the reaction is



The convention here is to write the oxidised form first and then followed by the reduced form. These two forms form a couple, written as 'Cu²⁺/Cu couple' or 'Zn²⁺/Zn couple'.

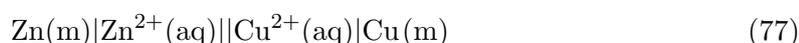
7.1.2 Cell Conventions

The conventions according to the lecture notes are

1. The LHS and RHS half cells should be clearly identified
2. Each half cell reaction is written as a reduction
3. Full reaction is found by RHS half cell reaction minus LHS half cell reaction
4. The cell potential is that of the RHS measured relative to the LHS

7.1.3 Cell Notations

The above reaction is express as follows



Note that ‘|’ is used to separate different phases; a comma is used to separate species in the same phase; ‘||’ indicates a junction between two solutions (often separate the two half cells).

7.2 Thermodynamic Parameters from Cell Potentials

By 1st Law, we know that $dU = TdS - pdV$, but when we introduce other forms of energy $\delta\varepsilon$ (e.g. electric energy) into the system, then we have

$$dU = TdS - pdV + \delta\varepsilon \quad (78)$$

Using the master equations, we can show that

$$dG = \delta\varepsilon + Vdp - SdT \quad (79)$$

At constant p and T , we have

$$dG = \delta\varepsilon \quad (80)$$

Considering the cell, the electric energy under electric potential difference E carried by n moles of electrons is $-nFE$, where F is the Faraday constant. Then easily

$$\Delta_r G_{\text{cell}} = -nFE \quad (81)$$

for constant p and T .

For the entropy change in the cell, it is easy using the relationship by the master equations (i.e. $(\partial G/\partial T)_p = -S$) to obtain

$$\Delta_r S_{\text{cell}} = nF \left(\frac{\partial E}{\partial T} \right)_p \quad (82)$$

Then $\Delta_r H_{\text{cell}}$ is easy to get.

7.3 Nernst Equation

7.3.1 Chemical Potentials and Activities

Remind yourself about the chemical potentials discussed earlier. The problem is that the solutions are in fact not ideal. Therefore, we need to introduce another quantity, called *activity* a_i , to formulate chemical potentials valid for real solutions

$$\mu_i(a_i) = \mu_i^\ominus + RT \ln a_i \quad (83)$$

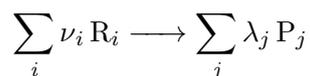
The activities satisfy the following property

$$a_i \rightarrow \left(\frac{c_i}{c^\ominus}\right) \text{ as } c_i \rightarrow 0 \quad (84)$$

For this course, most of the times, we may still use concentrations to approximate the activities.

7.3.2 Nernst Equation

Still, for the general reaction



similar to the derivations earlier, we have

$$\Delta_r G_{\text{cell}} = \Delta_r G_{\text{cell}}^\ominus + RT \ln \frac{\prod_j (a(\text{P}_j))^{\lambda_j}}{\prod_i (a(\text{R}_i))^{\nu_i}} \quad (85)$$

We denote

$$\Delta_r G_{\text{cell}}^\ominus = -nFE^\ominus \quad (86)$$

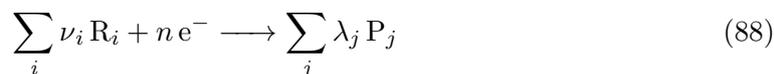
then it is easy to show

$$E = E^\ominus - \frac{RT}{nF} \ln \frac{\prod_j (a(\text{P}_j))^{\lambda_j}}{\prod_i (a(\text{R}_i))^{\nu_i}} \quad (87)$$

which is known as the *Nernst Equation*.

7.3.3 Nernst Equation for Half Cells

For the general half cell equation



the half-cell potential is given by

$$E_{1/2} = E_{1/2}^\ominus - \frac{RT}{nF} \ln \frac{\prod_j (a(\text{P}_j))^{\lambda_j}}{\prod_i (a(\text{R}_i))^{\nu_i}} \quad (89)$$

For the whole reaction, we have

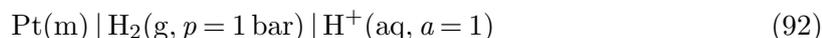
$$E = E_{1/2}(\text{RHS}) - E_{1/2}(\text{LHS}) \quad (90)$$

and

$$E^\ominus = E_{1/2}^\ominus(\text{RHS}) - E_{1/2}^\ominus(\text{LHS}) \quad (91)$$

7.4 Standard Half-Cell Potentials

The standard potentials of different half cells can be tabulated by setting up a standard electrode and measure the standard potential difference between the interested half cell and the standard one. The electrode whose standard potential is taken as zero is the *standard hydrogen electrode* (SHE). It is expressed in the cell notations as



Half cell equation is



The temperature of tabulation is often 298 K.

7.5 Spontaneous Cell Reaction

The spontaneous cell reaction is found by inspecting the sign of the cell potential. The reaction takes place when the current is allowed to flow

EXAMPLE. For cell



the potential developed is

$$E = E^\ominus(\text{Zn}^{2+}, \text{Zn}) - E^\ominus(\text{Cu}^{2+}, \text{Cu}) = -0.76 - (+0.34) = -1.10 \text{ V}$$

So the conventional reaction here is



but the spontaneous reaction is



7.6 Types of Half Cells

- **Metal/Metal Ion** These consist of a metal in contact with a solution of its ions
- **Gas/Ion** These consist of the gas in contact with a solution containing related ions; an inert Pt electrode provides the electrical contact. The ions can be anions or cations
- **Redox** The oxidised and reduced species are both present in solution; an inert Pt electrode provides the electrical contact
- **Metal/Insoluble Salt/Anion** These consist of a metal coated with a layer of the insoluble salt formed by the metal and the anion which is in the solution. The point about all of these electrodes is that their half-cell potentials depend on the concentrations of anions

7.7 Assessing Redox Stability Using Electrode Potentials

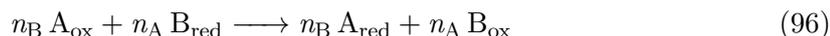
For some general redox reaction, we have RHS cell reaction



and LHS reaction



Take RHS - LHS, we have the conventional equation

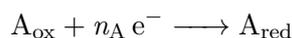


and the cell potential is

$$E = E^\ominus(A_{\text{ox}}, A_{\text{red}}) - E^\ominus(B_{\text{ox}}, B_{\text{red}}) \quad (97)$$

Therefore, it is easy to see, if $E^\ominus(A_{\text{ox}}, A_{\text{red}}) > E^\ominus(B_{\text{ox}}, B_{\text{red}})$, A_{ox} oxidises B_{red} ; if $E^\ominus(A_{\text{ox}}, A_{\text{red}}) < E^\ominus(B_{\text{ox}}, B_{\text{red}})$, A_{red} reduces B_{ox}

Also for



- The more positive the half cell potential, the more strongly oxidising A_{ox} is
- The more negative the half cell potential, the more strongly reducing A_{red} is

Unless we are comparing redox couples with similar standard potentials, the fact that the concentration we are dealing with are not the standard concentrations will not be of any great significance.

7.8 Applications

Using cell potentials, we can investigate solubility of ionic compounds, determine the thermodynamic parameters of ions, etc.

References

- [1] J. Keeler, Lent 2018, *Energetics and Equilibria*, Department of Chemistry, University of Cambridge