

14.3: Molar Reaction Quantities of the Cell Reaction

This e-book will denote the molar reaction Gibbs energy of a cell reaction by $\Delta_r G_{\text{cell}}$. This notation distinguishes it from the molar reaction Gibbs energy $\Delta_r G$ of the direct reaction, which may have a different value because in the cell the chemical potential of an ionic species is affected by the electric potential of its phase. $\Delta_r G_{\text{cell}}$ is defined by

$$\Delta_r G_{\text{cell}} \stackrel{\text{def}}{=} \sum_i \nu_i \mu_i \quad (14.3.1)$$

where the sum is over the reactants and products of the cell reaction. $\Delta_r G_{\text{cell}}$ is also equal to the partial derivative $(\partial G_{\text{cell}} / \partial \xi)_{T,p}$, where ξ is the advancement of the cell reaction.

14.3.1 Relation between $\Delta_r G_{\text{cell}}$ and $E_{\text{cell, eq}}$

When a galvanic cell is in a zero-current equilibrium state, both electrode reactions are at reaction equilibrium. In the electrode reaction at the left electrode, electrons are a product with stoichiometric number equal to z . At the right electrode, electrons are a reactant with stoichiometric number equal to $-z$. We can write the conditions for electrode reaction equilibria as follows:

$$\text{At the left electrode} \quad \sum_i \nu_i \mu_i + z \mu_e(\text{LE}) = 0 \quad (14.3.2)$$

$$\text{At the right electrode} \quad \sum_j \nu_j \mu_j - z \mu_e(\text{RE}) = 0 \quad (14.3.3)$$

In these equations, the sum over i is for the chemical species (excluding electrons) of the electrode reaction at the left electrode, and the sum over j is for the chemical species of the electrode reaction at the right electrode. $\mu_e(\text{LE})$ is the chemical potential of electrons in the electron conductor of the left electrode, and $\mu_e(\text{RE})$ is the chemical potential of electrons in the electron conductor of the right electrode.

Adding Eqs. 14.3.2 and 14.3.3, we obtain

$$\sum_i \nu_i \mu_i + \sum_j \nu_j \mu_j + z[\mu_e(\text{LE}) - \mu_e(\text{RE})] = 0 \quad (14.3.4)$$

The first two terms on the left side of Eq. 14.3.4 are sums over all the reactants and products of the cell reaction. From Eq. 14.3.1, we recognize the sum of these terms as the molar reaction Gibbs energy of the cell reaction:

$$\sum_i \nu_i \mu_i + \sum_j \nu_j \mu_j = \Delta_r G_{\text{cell}} \quad (14.3.5)$$

Substituting from Eq. 14.3.5 into Eq. 14.3.4 and solving for $\Delta_r G_{\text{cell}}$, we obtain

$$\Delta_r G_{\text{cell}} = -z[\mu_e(\text{LE}) - \mu_e(\text{RE})] \quad (14.3.6)$$

In a zero-current equilibrium state, there is electron transfer equilibrium between the left electron conductor and the left terminal, and between the right electron conductor and the right terminal: $\mu_e(\text{LE}) = \mu_e(\text{LT})$ and $\mu_e(\text{RE}) = \mu_e(\text{RT})$, where $\mu_e(\text{LT})$ and $\mu_e(\text{RT})$ are the chemical potentials of electrons in the left terminal and right terminal, respectively. Thus we can rewrite Eq. 14.3.6 as

$$\Delta_r G_{\text{cell}} = -z[\mu_e(\text{LT}) - \mu_e(\text{RT})] \quad (14.3.7)$$

Making substitutions from Eq. 14.2.2 for $\mu_e(\text{LT})$ and $\mu_e(\text{RT})$, and recognizing that $\mu_e(0)$ is the same in both terminals because they have the same composition, we obtain

$$\begin{aligned} \Delta_r G_{\text{cell}} &= -zF(\phi_R - \phi_L) \\ &= -zFE_{\text{cell, eq}} \end{aligned} \quad (14.3.8)$$

We can see from Eq. 14.3.1 that the value of $\Delta_r G_{\text{cell}}$ has nothing to do with the composition of the terminals. The relations of Eq. 14.3.8 were derived for a cell with both terminals made of the same metal. We can make the following deductions for such a cell:

1. Equation 14.3.8 can be derived by a different route. According to Eq. 5.8.6, reversible electrical work at constant T and p is equal to the Gibbs energy change: $dw_{\text{el, rev}} = dG_{\text{cell}}$. Making the substitution $dw_{\text{el, rev}} = E_{\text{cell, eq}} dQ_{\text{sys}}$ (from Eq. 3.8.8), with

dQ_{sys} set equal to $-zF d\xi$ (Eq. 14.1.1), followed by division by $d\xi$, gives $-zFE_{\text{cell, eq}} = (\partial G_{\text{cell}}/\partial \xi)_{T,p}$, or $\Delta_r G_{\text{cell}} = -zFE_{\text{cell, eq}}$.

Strictly speaking, this derivation applies only to a cell without a liquid junction. In a cell with a liquid junction, the electric current is carried across the junction by different ions depending on the direction of the current, and the cell is therefore not reversible.

14.3.2 Relation between $\Delta_r G_{\text{cell}}$ and $\Delta_r G$

Now imagine a reaction vessel that has the same temperature and pressure as the galvanic cell, and contains the same reactants and products at the same activities as in the cell. This reaction vessel, unlike the cell, is not part of an electrical circuit. In it, the reactants and products are in direct contact with one another, so there is no constraint preventing a spontaneous direct reaction. For example, the reaction vessel corresponding to the zinc–copper cell of Fig. 14.2 would have zinc and copper strips in contact with a solution of both ZnSO_4 and CuSO_4 . Another example is the slow direct reaction in a cell without liquid junction described in Sec. 14.2.1.

Let the reaction equation of the direct reaction be written with the same stoichiometric numbers ν_i as in the reaction equation for the cell reaction. The direct reaction in the reaction vessel is described by this equation or its reverse, depending on which direction is spontaneous for the given activities.

The question now arises whether the molar reaction Gibbs energy $\Delta_r G_{\text{cell}}$ of the cell reaction is equal to the molar reaction Gibbs energy $\Delta_r G$ of the direct reaction. Both $\Delta_r G_{\text{cell}}$ and $\Delta_r G$ are defined by the sum $\sum_i \nu_i \mu_i$. Both reactions have the same values of ν_i , but the values of μ_i for charged species are in general different in the two systems because the electric potentials are different.

Consider first a cell without a liquid junction. This kind of cell has a single electrolyte solution, and all of the reactant and product ions of the cell reaction are in this solution phase. The same solution phase is present in the reaction vessel during the direct reaction. When all ions are in the same phase, the value of $\sum_i \nu_i \mu_i$ is independent of the electric potentials of any of the phases (see the comment following Eq. 11.8.4), so that the molar reaction Gibbs energies are the same for the cell reaction and the direct reaction:

$$\Delta_r G_{\text{cell}} = \Delta_r G \quad (14.3.9)$$

(no liquid junction)

Next, consider a cell with two electrolyte solutions separated by a liquid junction. For the molar reaction Gibbs energy of the cell reaction, we write

$$\Delta_r G_{\text{cell}} = \sum_i \nu_i \mu_i(\phi_i) + \sum_j \nu_j \mu_j(\phi_j) \quad (14.3.10)$$

The sums here include all of the reactants and products appearing in the cell reaction, those with index i being at the left electrode and those with index j at the right electrode. Let the solution at the left electrode be phase α and the solution at the right electrode be phase β . Then making the substitution $\mu_i(\phi) = \mu_i(0) + z_i F \phi$ (Eq. 10.1.6) gives us

$$\Delta_r G_{\text{cell}} = \sum_i \nu_i \mu_i(0) + \sum_j \nu_j \mu_j(0) + \sum_i \nu_i z_i F \phi^\alpha + \sum_j \nu_j z_j F \phi^\beta \quad (14.3.11)$$

The sum of the first two terms on the right side of Eq. 14.3.11 is the molar reaction Gibbs energy of a reaction in which the reactants and products are in phases of zero electric potential. According to the comment following Eq. 11.8.4, the molar reaction Gibbs energy would be the same if the ions were in a single phase of any electric potential. Consequently the sum $\sum_i \nu_i \mu_i(0) + \sum_j \nu_j \mu_j(0)$ is equal to $\Delta_r G$ for the direct reaction.

The conservation of charge during advancement of the electrode reactions at the left electrode and the right electrode is expressed by $\sum_i \nu_i z_i - z = 0$ and $\sum_j \nu_j z_j + z = 0$, respectively. Equation 14.3.11 becomes

$$\Delta_r G_{\text{cell}} = \Delta_r G - zFE_j \quad (14.3.12)$$

(cell with liquid junction)

where $E_j = \phi^\beta - \phi^\alpha$ is the liquid junction potential.

Finally, in Eqs. 14.3.9 and 14.3.12 we replace $\Delta_r G_{\text{cell}}$ by $-zFE_{\text{cell, eq}}$ (Eq. 14.3.8) and solve for $E_{\text{cell, eq}}$:

$$E_{\text{cell, eq}} = -\frac{\Delta_r G}{zF} \quad (14.3.13)$$

(cell without liquid junction)

$$E_{\text{cell, eq}} = -\frac{\Delta_r G}{zF} + E_j \quad (14.3.14)$$

(cell with liquid junction)

$E_{\text{cell, eq}}$ can be measured with great precision. If a reaction can be carried out in a galvanic cell without liquid junction, Eq. 14.3.13 provides a way to evaluate $\Delta_r G$ under given conditions. If the reaction can only be carried out in a cell with a liquid junction, Eq. 14.3.14 can be used for this purpose provided that the liquid junction potential E_j can be assumed to be negligible or can be estimated from theory.

Note that the cell has reaction equilibrium only if $\Delta_r G$ is zero. The cell has thermal, mechanical, and transfer equilibrium when the electric current is zero and the cell potential is the zero-current cell potential $E_{\text{cell, eq}}$. Equations 14.3.13 and 14.3.14 show that in order for the cell to also have reaction equilibrium, $E_{\text{cell, eq}}$ must equal the liquid junction potential if there is a liquid junction, or be zero otherwise. These are the conditions of an exhausted, “dead” cell that can no longer do electrical work.

14.3.3 Standard molar reaction quantities

Consider a hypothetical galvanic cell in which each reactant and product of the cell reaction is in its standard state at unit activity, and in which a liquid junction if present has a negligible liquid junction potential. The equilibrium cell potential of this cell is called the **standard cell potential** of the cell reaction, $E_{\text{cell, eq}}^\circ$. An experimental procedure for evaluating $E_{\text{cell, eq}}^\circ$ will be described in Sec. 14.5.

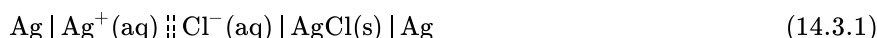
In this hypothetical cell, $\Delta_r G_{\text{cell}}$ is equal to the standard molar reaction Gibbs energy $\Delta_r G^\circ$. From Eq. 14.3.13, or Eq. 14.3.14 with E_j assumed equal to zero, we have

$$\Delta_r G^\circ = -zF E_{\text{cell, eq}}^\circ \quad (14.3.15)$$

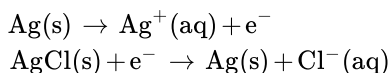
$\Delta_r G^\circ$ is the molar reaction Gibbs energy when each reactant and product is at unit activity and, if it is an ion, is in a phase of zero electric potential. Since $\Delta_r G^\circ$ is equal to $-RT \ln K$ (Eq. 11.8.10), we can write

$$\ln K = \frac{zF}{RT} E_{\text{cell, eq}}^\circ \quad (14.3.16)$$

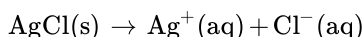
Equation 14.3.16 allows us to evaluate the thermodynamic equilibrium constant K of the cell reaction by a noncalorimetric method. Consider for example the cell



in which the pair of dashed vertical bars indicates a liquid junction of negligible liquid junction potential. The electrode reactions are



and the cell reaction is



The equilibrium constant of this reaction is the solubility product K_s of silver chloride (Sec. 12.5.5). At 298.15 K, the standard cell potential is found to be $E_{\text{cell, eq}}^\circ = -0.5770$ V. We can use this value in Eq. 14.3.16 to evaluate K_s at 298.15 K (see Prob. 14.5).

Equation 14.3.16 also allows us to evaluate the standard molar reaction enthalpy by substitution in Eq. 12.1.13:

$$\begin{aligned} \Delta_r H^\circ &= RT^2 \frac{d \ln K}{dT} \\ &= zF \left(T \frac{d E_{\text{cell, eq}}^\circ}{dT} - E_{\text{cell, eq}}^\circ \right) \end{aligned} \quad (14.3.17)$$

(no solute standard states based on concentration)

Finally, by combining Eqs. 14.3.15 and 14.3.17 with $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we obtain an expression for the standard molar reaction entropy:

$$\Delta_r S^\circ = zF \frac{dE_{\text{cell, eq}}^\circ}{dT} \quad (14.3.18)$$

(no solute standard states
based on concentration)

Because G , H , and S are state functions, the thermodynamic equilibrium constant and the molar reaction quantities evaluated from $E_{\text{cell, eq}}^\circ$ and $dE_{\text{cell, eq}}^\circ/dT$ are the same quantities as those for the reaction when it takes place in a reaction vessel instead of in a galvanic cell. However, the heats at constant T and p are not the same (Sec. 11.3.1). During a reversible cell reaction, dS must equal $\delta q/T$, and $\delta q/d\xi$ is therefore equal to $T\Delta_r S^\circ$ during a cell reaction taking place reversibly under standard state conditions at constant T and p .

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