EMF AND THERMODYNAMIC MAGNITUDES
OF THE GALVANIC CELLS

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ABSTRACT: Many textbooks on experimental Physical Chemistry show how $\Delta G$, $\Delta H$ and $\Delta S$ of a chemical reaction can be calculated from the emf of the corresponding galvanic cell. In these experiments, $\Delta G = nFE$ is simply stated. However, attention must be paid to the meaning of such quantities when reactants and products of the reaction are not in their standard states. In this case, $\Delta G$, $\Delta H$ and $\Delta S$ refer to the change in the Gibbs energy, enthalpy and entropy of the system when a mole of product is formed, the activities of reactants and products being those of the actual cell and the system having sufficient mass to remain at constant composition. The emf of this cell is equal to $E^0$ and thus, $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ can be directly calculated, only when reactants and products are in their standard states. In the case that reactants and products were not in their standard states, $E^0$ should be determined from the emf measurements by an extrapolation method because $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ are the relevant magnitudes in Thermodynamics.

KEYWORDS: Galvanic cells; thermodynamic magnitudes.

Introduction

In the most part of the experimental textbooks of Physical Chemistry, experiments in which the main object is to obtain the thermodynamic magnitudes $\Delta G$, $\Delta H$ and $\Delta S$ of a chemical reaction from emf measurements of a galvanic cell can be found.\textsuperscript{4, 6, 10, 12, 15, 16, 18, 20, 21} It is well known that the galvanic cells present a great importance in determining the thermodynamic properties of the chemical systems. In particular, it is always theoretically possible to design a galvanic cell in which the corresponding chemical reaction coincides with the reaction of interest: a) electron or ion exchange reactions; b) complex, insoluble salt or neutral species formation or c) reactions in which a concentration change is simply concerned.

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The anodic and cathodic reactions can be written, respectively,

\[ \text{A} + \text{B} \rightarrow \text{A} \cdot \text{B} \]

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the total reaction of the cell being

\[ \text{A} + \text{B} \rightarrow \text{A}_x \cdot \text{B}_y \]

When, at constant pressure and temperature, the terminals of the galvanic cell are connected to a voltmeter with sufficiently high impedance, the total current which passes through the circuit is negligible and the composition of the system, evolving only in the formation of the product in Eq. (1) if the end of the galvanic cell is positive, only in the formation of the product in Eq. (3) if the end of the galvanic cell is negative, with the reverse value in an infinitesimal quantity. Such a composition change takes place with the production of an infinitesimal electrical work.

\[ \omega = \frac{E \cdot dQ}{(k - h)} \]

where \( E \) is the end of the cell, given in volts, \( k \) is the potential difference between the right (potential being \( h \)) and the left terminal (potential of \( k \) of the external circuit.

\[ \omega = \frac{E \cdot dQ}{(k - h)} \]

The decrease in the Gibbs energy gives, at constant temperature and pressure,

\[ \Delta S = \frac{E}{T} \cdot dQ \]

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where the minus sign appears because\( E \cdot dQ \) is the work produced by the system, that is the system has lost such a quantity of energy.

On the other hand, it is well known that for an elementary process in a system in thermodynamic (scenarios in which the concept of absolute entropy is used), the reaction equation can be easily followed.

\[ \Delta S = \frac{E}{T} \cdot dQ \]

From Eqs. (9) and (10) it follows that:

\[ \Delta S = \frac{E}{T} \cdot dQ \]

The derivation of the basic equations

Let us suppose the galvanic cell

\[ \text{Me}^{+}(\text{aq}) + e\rightarrow \text{Me}^{0} \]

in which \( \text{Me}^{+} \) (and \( \text{Me}^{0} \) denote a common ionic salt, the anodic reaction (negative) and the cathodic reaction (positive) of the cell. We will also suppose that there is not any liquid junction, that is the system in the same phase. However, if a liquid junction is necessary in order not to mix the reactants of the anode and the cathode, the liquid junction potential can be replaced by means of a suitable salt bridge (in this case, the transport index of the dissolved species do not appear in any equation in the description of the galvanic cell).
It is clear that the infinitesimal charge which passes through the external circuit, \( dq \), and the infinitesimal change in the moles of the species involved in reaction (6c), \( \Delta n_i \), are not independent. They are related through the extent of the reaction. The extent of the reaction, \( \xi \), of reaction (6c) is given by:

\[
\xi = \frac{(n_i - n_f)}{v_i} \quad \text{(mol)}
\]  

(12)

where \( n_i \) is the number of moles of the species \( i \) which are actually present in the system, \( n_f \) the initial number of moles of the species \( i \) and \( v_i \) the stoichiometric coefficient of the species \( i \) in reaction (6c). It should be noted that \( v_i \) is positive for the products and negative for the reactants of the corresponding reaction. The stoichiometric coefficient is a dimensionless quantity which assures that the number of atoms involved in the reaction are constant. Note that each particular value of \( \xi \) means a specific composition.

Eq. (12), written for an infinitesimal change, takes the form:

\[
dn_i = v_i \, d\xi \quad \text{(mol)}
\]  

(13)

As the stoichiometric coefficient of the electrons in reactions (6a) and (6c) is \( n \), the moles of electrons which pass through the circuit for an infinitesimal change in the moles of the species \( dn_i \) are given by \( n \, d\xi \) and therefore, the infinitesimal charge will take the form:

\[
dq = nF \, d\xi \quad \text{(Coulombs)}
\]  

(14)

\( F \) being the Faraday constant (96485 C per mole of electrons).

Introducing Eqs. (13) and (14) in Eq. (11), one obtains:

\[
dG_{P,T} = -nFE \, d\xi = \sum \mu_i \, d\xi \quad \text{(joules)}
\]  

(15)

From Eq. (15) it follows that:

\[
\frac{dG}{d\xi}_{P,T} = -nFE = \sum \mu_i \quad \text{(joules mol\(^{-1}\))}
\]  

(16)

When Eqs. (1) and (16) are compared, it follows that \( \Delta G(P,T) \) in Eq. (1) is not the change in the Gibbs energy of the reaction at constant pressure and temperature, but the slope of the \( G \) vs. \( \xi \) plot at constant pressure and temperature, where

\[
G_{P,T} = \sum n_i \, \mu_i
\]  

(17)

This is what makes sense of the chemical affinity of the reaction, \( \mathcal{A} \), which is equal to:

\[
\mathcal{A} = -\left( \frac{\partial G}{\partial \xi} \right)_{P,T}
\]  

(18)

When \( \mathcal{A} \) is greater than zero, i.e., when \( E \) is positive and \( \sum v_i \, \mu_i \) negative, the chemical reaction associated with the galvanic cell is spontaneous.

If the Gibbs-Helmholtz equation

\[
G = H + T \left( \frac{\partial G}{\partial T} \right)_{P,N}
\]  

(19)

where \( N \) means constant composition, is derived with respect to \( \xi \) at constant temperature and pressure, and the result introduced in Eq. (16), one obtains:

\[
\left( \frac{\partial H}{\partial \xi} \right)_{P,T} = \left[ (\partial G/\partial \xi)_{P,T} - T((\partial G/\partial T)_{P,N}) \right]_{P,T} = \left[ (\partial G/\partial \xi)_{P,T} - T((\partial G/\partial T)_{P,N}) \right]_{P,T} = -nF \left( E - T \left( \frac{\partial E}{\partial T} \right)_{P,N} \right)
\]  

(20)

Similarly, as the entropy is equal to

\[
S = -\left( \frac{\partial G}{\partial T} \right)_{P,N}
\]  

(21)

one obtains:

\[
\left( \frac{\partial S}{\partial \xi} \right)_{P,T} = \left[ ((\partial G/\partial \xi)_{P,T} - T((\partial G/\partial T)_{P,N}) \right]_{P,T} = \left[ ((\partial G/\partial \xi)_{P,T} - T((\partial G/\partial T)_{P,N}) \right]_{P,T} = nF \left( \frac{\partial E}{\partial T} \right)_{P,N}
\]  

(22)

and therefore, \( \Delta H(P,T) \) and \( \Delta S(P,T) \) in Eq. (2) are the slope of the \( H \) vs. \( \xi \) plot and the slope of the \( S \) vs. \( \xi \) plot, respectively, at constant pressure and temperature, not the enthalpy of the reaction nor the entropy change when the reaction takes place, as could be assumed from Eq. (2).

Eqs. (1) to (3) are only true when they refer to the standard quantities. In this case, when writing the chemical potential as:

\[
\mu_i = \mu_i^0 + RT \ln a_i
\]  

(23)

and introducing Eq. (23) in Eq. (16), it follows that:

\[
\sum v_i \, \mu_i = \sum v_i \, \mu_i^0 + RT \ln \Pi a_i
\]  

(24)

It is clear from Eqs. (16) and (24) that:

\[
\Delta G^0 = \sum v_i \, \mu_i^0 = -nFE
\]  

(25)
\[ \Delta S^\circ = - (\partial \Delta G^\circ / \partial T)_P \]  
(26)

\[ \Delta H^\circ = \Delta G^\circ + T \Delta S^\circ \]  
(27)

it follows that:

\[ \Delta H^\circ = -nF(E^\circ - T(\partial E^\circ / \partial T)) \]  
(28)

\[ \Delta S^\circ = nF(\partial E^\circ / \partial T) \]  
(29)

**Conclusion**

It is therefore concluded that Eqs. (1) to (3) are only valid when all the given thermodynamic data correspond to reactants and products in their standard states and then, the standard Gibbs energy and the standard enthalpy of the reaction, as well as the change in the standard entropy of the system, can be determined. If the reactants and products of the reaction associated with the galvanic cell are not in their standard states, one can then only obtain the change in the Gibbs energy, enthalpy and entropy of the system when it suffers a chemical reaction in which a mole of product is formed, the system having sufficient mass (virtually infinite) to remain at constant composition. Anyway, \( E^\circ \) can be obtained from emf measurements of galvanic cells having different compositions and employing the usual extrapolation methods. The general conclusion is that attention must be paid to the correct interpretation of the thermodynamic quantities obtained by Eqs. (1) to (3) when the chemical reaction associated with the galvanic cell involves reactants and products which are not in their standard states.

**References**


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