

EMF AND THERMODYNAMIC MAGNITUDES OF THE GALVANIC CELLS

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■ **ABSTRACT:** Many textbooks on experimental Physical Chemistry show how ΔG , ΔH and ΔS 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, ΔG , ΔH and ΔS 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 the cell is equal to E° and thus, ΔG° , ΔH° and ΔS° 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° should be determined from the *emf* measurements by an extrapolation method because ΔG° , ΔH° and ΔS° 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 ΔG , ΔH and ΔS of a chemical reaction from *emf* measurements of a galvanic cell can be found.^{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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In order to obtain the values of ΔG , ΔH and ΔS for a given chemical reaction from *emf* (E) and $(\partial E/\partial T)_P$ measurements and the equations

$$\Delta G_i(P, T) = -nFE \quad (1)$$

$$\Delta H_i(P, T) = -nF[E - T(\partial E/\partial T)_P] \quad (2)$$

$$\Delta S_i(P, T) = nF(\partial E/\partial T)_P \quad (3)$$

the galvanic cell should be reversible, that is the electrodes should be reversible and no liquid junctions should exist. This is not always strictly fulfilled in the experiments of the literature.

Eqs. (1-3) are demonstrated in many books of Physical Chemistry and of Chemical Thermodynamics.^{2, 3, 8, 11, 14, 17} In addition, Eqs. (1-3) have a great historical importance. They were applied by Richards (1902) to obtain the dependence of ΔG on the temperature and extrapolated later by Nernst (1906) to establish the Heat Theorem:

$$\lim_{T \rightarrow 0} \frac{d(\Delta G)/dT}{T} = \lim_{T \rightarrow 0} \frac{d(\Delta H)/dT}{T} \quad (4)$$

which finally led to the practical scale of absolute entropies of the Third Law of Thermodynamics.

However, it should be noted that the symbols ΔG_i , ΔH_i and ΔS_i of Eqs. (1-3) have different meaning from that normally assigned to the operator Δ , that is the difference between the value of the thermodynamic magnitudes between two states of the system.^{1, 4, 7, 9, 13, 19} This conceptually important observation can be easily followed paying attention to the derivation of Eqs. (1-3).

Derivation of the basic equations

Let's suppose the galvanic cell



in which $\text{Me}(-)$ and $\text{Me}(+)$ mean a common inert metal providing the electrons for the anodic reaction (negative pole) and the cathodic reaction (positive pole). We will also suppose that there is not any liquid junctions, that is the soluble species coexist 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 neglected by means of a suitable salt bridge (in this case, the transport index of the dissolved species do not appear in the *emf* equation of the galvanic cell).

The anodic and cathodic reactions can be written, respectively:



the total reaction of the cell being:



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 to the formation of products in Eq. (6c) if the *emf* of the galvanic cell is positive, only varies in an infinitesimal quantity. Such a composition change takes place with the production of an infinitesimal electrical work:

$$\omega = E dQ \quad (7)$$

where E is the *emf* of the cell, given in volts and defined as the potential difference between the right (its potential being ϕ_R) and the left terminal (potential of ϕ_L) of the cell when the intensity which passes through the system tends to zero:

$$E = \lim_{I \rightarrow 0} (\phi_R - \phi_L) \quad (8)$$

and dQ , given in coulombs, is the infinitesimal charge which passes through the external circuit.

The decrease in the Gibbs energy gives, at constant temperature and pressure, the reversible electrical work received from the system:

$$dG_{P,T} = -E dQ \quad (\text{given in Joules}) \quad (9)$$

where the minus sign appears because $E dQ$ 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 mechanical and thermal equilibrium which undergoes reaction (6c):

$$dG_{P,T} = \sum \mu_i dn_i \quad (\text{Joules}) \quad (10)$$

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

$$dG_{P,T} = -E dQ = \sum \mu_i dn_i \quad (\text{Joules}) \quad (11)$$

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), dn_i , are not independent. They are related through the extent of the reaction. The extent of the reaction, ξ , of reaction (6c) is given by:

$$\xi = (n_i - n_{i0}) / \nu_i \quad (\text{mol}) \quad (12)$$

where n_i is the number of moles of the species i which are actually present in the system, n_{i0} the initial number of moles of the species i and ν_i the stoichiometric coefficient of the species i in reaction (6c). It should be noted that ν_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 ξ means a specific composition.

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

$$dn_i = \nu_i d\xi \quad (\text{mol}) \quad (13)$$

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:

$$dQ = nF d\xi \quad (\text{Coulombs}) \quad (14)$$

F being the Faraday constant (96486 C per mole of electrons).

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

$$dG_{P,T} = -nFE d\xi = \sum \nu_i \mu_i d\xi \quad (\text{Joules}) \quad (15)$$

From Eq. (15) it follows that:

$$(\partial G / \partial \xi)_{P,T} = -nFE = \sum \nu_i \mu_i \quad (\text{Joules mol}^{-1}) \quad (16)$$

When Eqs. (1) and (16) are compared, it follows that $\Delta G_r(P,T)$ 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. ξ plot at constant pressure and temperature, where

$$G_{P,T} = \sum n_i \mu_i \quad (17)$$

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

$$\mathcal{A} = -(\partial G / \partial \xi)_{P,T} \quad (18)$$

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

If the Gibbs-Helmholtz equation

$$G = H + T (\partial G / \partial T)_{P,N} \quad (19)$$

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

$$\begin{aligned} (\partial H / \partial \xi)_{P,T} &= (\partial G / \partial \xi)_{P,T} - T[(\partial / \partial \xi)(\partial G / \partial T)_{P,N}]_{P,T} = \\ &= (\partial G / \partial \xi)_{P,T} - T[(\partial / \partial T)(\partial G / \partial \xi)_{P,T}]_{P,N} = \\ &= -nF [E - T(\partial E / \partial T)_{P,N}] \end{aligned} \quad (20)$$

Similarly, as the entropy is equal to

$$S = -(\partial G / \partial T)_{P,N} \quad (21)$$

one obtains:

$$\begin{aligned} (\partial S / \partial \xi)_{P,T} &= -[(\partial / \partial \xi)(\partial G / \partial T)_{P,N}]_{P,T} = \\ &= -[(\partial / \partial T)(\partial G / \partial \xi)_{P,T}]_{P,N} = \\ &= nF (\partial E / \partial T)_{P,N} \end{aligned} \quad (22)$$

and therefore, $\Delta H_r(P,T)$ and $\Delta S_r(P,T)$ in Eq. (2) are the slope of the H vs. ξ plot and the slope of the S vs. ξ 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:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (23)$$

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

$$\sum \nu_i \mu_i = \sum \nu_i \mu_i^\circ + RT \ln \prod a_i^{\nu_i} \quad (24)$$

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

$$\Delta G_r^\circ = \sum \nu_i \mu_i^\circ = -nFE^\circ \quad (25)$$

and therefore, using

$$\Delta S^{\circ} = -(\partial \Delta G^{\circ} / \partial T)_p \quad (26)$$

$$\Delta H^{\circ} = \Delta G^{\circ} + T \Delta S^{\circ} \quad (27)$$

it follows that:

$$\Delta H_f^{\circ} = -nF[E^{\circ} - T(\partial E^{\circ} / \partial T)_p] \quad (28)$$

$$\Delta S_f^{\circ} = nF(\partial E^{\circ} / \partial T)_p \quad (29)$$

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° 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.

PÉREZ, E., CABOT, P. L. Força eletromotriz e grandezas termodinâmicas das células galvânicas. *Ecl. Quim.* (São Paulo), v.21, p.125-132, 1996.

■ **RESUMO:** Muitos textos de Físico-Química Experimental mostram como ΔG , ΔH e ΔS de uma reação química podem ser calculados a partir da força eletromotriz (f.e.m.) de células galvânicas. Nesses experimentos considera-se $\Delta G = -nFE$. Entretanto, deve-se levar em conta o significado dessas quantidades quando os reagentes e os produtos da reação não se encontram em seus estados-padrão. Neste caso, ΔG , ΔH e ΔS correspondem às mudanças na energia de Gibbs, na entalpia e na entropia do sistema quando 1 mol do produto é formado, com as atividades dos reagentes e dos produtos correspondendo àquelas da célula real e com o sistema possuindo massa suficiente para permanecer com composição constante. A f.e.m. da célula é igual a E° e então ΔG° , ΔH° e ΔS° só podem ser calculados diretamente quando os reagentes e os produtos da reação estão em seus estados-padrão. Quando isso não ocorre, E° deve ser determinado, a partir de medidas da f.e.m., por um método de extrapolação, porque ΔG° , ΔH° e ΔS° são as grandezas relevantes na Termodinâmica.

■ **PALAVRAS-CHAVE:** Células galvânicas; grandezas termodinâmicas.

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Recebido em 19.2.1996.

Aceito em 28.3.1996.