

Conference materials

UDC 544

DOI: <https://doi.org/10.18721/JPM.161.146>

### Equilibrium shift in chemical reactions

N.A. Charykov<sup>1,2</sup>, V.V. Kuznetsov<sup>1✉</sup>, W. Sadowski<sup>3</sup>, K.N. Semenov<sup>4</sup>,  
V.A. Keskinov<sup>2</sup>, A.A. Blokhin<sup>2</sup>, D.G. Letenko<sup>5</sup>, Z.K. Shamardanov<sup>6</sup>,  
B.K. Shaymardanova<sup>6</sup>, N.A. Kulenova<sup>6</sup>, M.A. Sadenova<sup>6</sup>

<sup>1</sup> St. Petersburg Electrotechnical University "LETI", St. Petersburg, Russia;

<sup>2</sup> St. Petersburg Institute of Technology (Technical University), St. Petersburg, Russia;

<sup>3</sup> Gdańsk University of Technology, Gdańsk, Poland;

<sup>4</sup> Academician I.P. Pavlov First St. Petersburg State Medical University, St. Petersburg, Russia;

<sup>5</sup> St. Petersburg State University of Architecture and Civil Engineering, St. Petersburg, Russia;

<sup>6</sup> East Kazakhstan State Technical University, Center "Veritas" Ust-Kamenogorsk, Republic of Kazakhstan

✉ [vvkuznetsov@inbox.ru](mailto:vvkuznetsov@inbox.ru)

**Abstract.** An original approach for describing chemical equilibrium shifts in systems of any physico-chemical nature has been developed. The mathematical expression of the equilibrium principle as formulated by the authors contains, instead of the standard heat and volume changes during a chemical reaction, mixing functions that in some special cases exceed the standard ones. It is shown that in systems with extremely large deviations from ideality (for example, in aqueous solutions of uranyl salts or water-soluble light fullerenes derivatives) the equilibrium shift principle developed by the authors may fundamentally differ from the well-known Le Chatelier-Brown principle).

**Keywords:** chemical equilibrium, Le Chatelier-Brown principle

**Funding:** This research has been supported by the Project of Russian Scientific Found (Project № 23-23-00064) and Project of IRN BR10965186 "Development and implementation of geo-information support for "smart" agriculture to improve the management of the agro-industrial complex", funded by the Science Committee of The Ministry of Education and Science of the Republic of Kazakhstan.

**Citation:** Charykov N.A., Kuznetsov V.V., Sadowski W., Semenov K.N., Keskinov V.A., Blokhin A.A., Letenko D.G., Shamardanov Z.K., Shaymardanova B.K., Kulenova N.A., Sadenova M.A., Equilibrium Shift in Chemical Reactions, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (1.1) (2023) 275–280. DOI: <https://doi.org/10.18721/JPM.161.146>

This is an open access article under the CC BY-NC 4.0 license (<https://creativecommons.org/licenses/by-nc/4.0/>)

Материалы конференции

УДК 544

DOI: <https://doi.org/10.18721/JPM.161.146>

### Смещение равновесия при химической реакции

Н.А. Чарыков<sup>1,2</sup>, В.В. Кузнецов<sup>1✉</sup>, В. Садовски<sup>3</sup>, К.Н. Семенов<sup>4</sup>,  
В.А. Кескинов<sup>2</sup>, А.А. Блохин<sup>2</sup>, Д.Г. Летенко<sup>5</sup>, Ж.К. Шамарданов<sup>6</sup>,  
Б.К. Шамарданова<sup>6</sup>, Н.А. Куленова<sup>6</sup>, М.А. Саденова<sup>6</sup>

<sup>1</sup> Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова (Ленина), Санкт-Петербург, Россия;

<sup>2</sup> Санкт-Петербургский государственный технологический институт (технический университет) Санкт-Петербург, Россия;

<sup>3</sup> Гданьский политехнический университет, г. Гданьск, Польша;

<sup>4</sup> Первый Санкт-Петербургский государственный медицинский университет им. академика И.П. Павлова, Санкт-Петербург, Россия;

<sup>5</sup> Санкт-Петербургский государственный архитектурно-строительный университет, Санкт-Петербург, Россия;

<sup>6</sup> Восточно-Казахстанский государственный технический университет, Центр «Веритас», г. Усть-Каменогорск, Республика Казахстан

✉ vvkuznetsov@inbox.ru

**Аннотация.** Разработан оригинальный метод описания сдвигов химического равновесия в системах произвольной физико-химической природы. Математическое выражение принципа в формулировке авторов содержит вместо стандартных теплот и изменений объемов в ходе химической реакции функции смещения, которые в некоторых особых случаях превосходят стандартные. Показано, что в системах с экстремально большими отклонениями от идеальности (например, в водных растворах солей уранила или водорастворимых производных легких фуллеренов) разработанный авторами принцип смещения равновесия может кардинально отличаться от известного принципа Ле Шателье-Брауна.

**Ключевые слова:** химическое равновесие, принцип Ле-Шателье-Брауна

**Финансирование:** Исследование выполнено при поддержке Проекта Российского научного фонда (проект № 23-23-00064) и Проекта ИРН BR10965186 «Разработка и внедрение геоинформационного обеспечения «умного» сельского хозяйства для улучшения управления агропромышленным комплексом», финансируемого Комитетом науки Министерства образования и науки Республики Казахстан.

**Ссылка при цитировании:** Чарыков Н.А., Кузнецов В.В., Садовски В., Семенов К.Н., Кескинов В.А., Блохин А.А., Летенко Д.Г., Шамарданов Ж.К., Шамарданова Б.К., Куленова Н.А., Саденова М.А. Смещение равновесия при химической реакции // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 1.1. С. 275–280. DOI: <https://doi.org/10.18721/JPM.161.146>

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>)

## Introduction

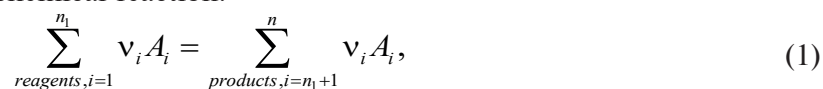
The conditions of chemical equilibrium shifts in the systems with single chemical reaction were elaborated in the classical thermodynamic works and are well known as Le Chatelier-Brown principle or simply Le Chatelier principle. This principle was repeatedly supplemented, justified, and commented in a number of thermodynamic works, e.g., in classical monographs [1–8]. Except of the original author of the principle [9] the fundamental role of J.W. Gibbs should be noted in substantiating this principle [4–6].

The authors consider the presentation in the monograph [10] to be the most successful in terms of simplicity, consistency and generality.

## Materials and Methods

Let us consider isolated equilibrium reactions, where reactions have no common reagents or products, or isolated “free” reaction systems. This allows us to consider any reaction separately without taking into account other reactions.

Let us consider equilibrium chemical reaction:



where  $\nu_i$  is stoichiometric coefficient of molecular  $A_i$  in reaction (1),  $n_1$  and  $n$  are number of reagents and number of all participants in the reaction (1). Assume that

$$\nu_i < 0 \text{ for reagents } 1 \leq i \leq n_1; \nu_i > 0 \text{ for products } n_1 \leq i \leq n \quad (2)$$

© Чарыков Н.А., Кузнецов В.В., Садовски В., Семенов К.Н., Кескинов В.А., Блохин А.А., Летенко Д.Г., Шамарданов Ж.К., Шамарданова Б.К., Куленова Н.А., Саденова М.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



So, we can simplify eq.(1) to

$$\sum_{i=1}^n \nu_i A_i = 0. \quad (3)$$

Differential equation of chemical equilibrium conservation will be the following:

$$\sum_{i=1}^n \nu_i d\mu_i = 0. \quad (4)$$

Differentiating equation (4) by temperature ( $T$ ), pressure ( $P$ ) and molar number of all components ( $n_i$ ) we get the expression:

$$-\Delta S^{(r)} dT + \Delta V^{(r)} dP - \Delta A f^{(r)} d\xi = 0, \quad (5)$$

where:

$$\Delta S^{(r)} = \sum_{i=1}^n \nu_i S_i, \quad (6)$$

$$\Delta V^{(r)} = \sum_{i=1}^n \nu_i V_i, \quad (7)$$

$$\Delta A f^{(r)} d\xi = \sum_{i=1}^n \nu_i (d\mu_i)_{P,T} = \sum_{i=1}^n \sum_{j=1}^n \nu_i \nu_j G_{ij} d\xi, \quad (8)$$

$$\Delta G^{(r)} = \sum_{i=1}^n \nu_i \mu_i = 0, \quad (9)$$

$$\Delta H^{(r)} = \sum_{i=1}^n \nu_i H_i. \quad (10)$$

In eq.(6–10)

$$S_i = -(d\mu_i / dT)_{P, n_{j \neq i}}, \quad (11)$$

$$V_i = (d\mu_i / dP)_{T, n_{j \neq i}}; H_i = \mu_i + TS_i, \quad (12)$$

are partial molar entropy, partial molar volume and enthalpy of  $i$ -th component, respectively;  $\Delta A f^{(r)}$  is chemical affinity of reaction (3),  $\xi$  is chemical variable,  $G_{ij} = (\partial^2 G / \partial n_i \partial n_j)_{T, P, n_{k \neq i, j}}$ . According to physical sense,  $\Delta S^{(r)}$ ,  $\Delta V^{(r)}$ ,  $\Delta A^{(r)}$ ,  $\Delta G^{(r)}$  are change of entropy, volume, chemical affinity and Gibbs energy, respectively, in the isotherm-isobaric process of the formation of  $\nu_i$  moles of product  $A_i (i = n_1 + 1, n_1 + 2, \dots, n)$  from  $\nu_i$  moles of reagent  $A_i (i = 1, 2, \dots, n_1)$  in the mixed phase (or phases) with infinitely large mass, which contains both reagents and products. According to the sense of  $\xi$ :

$$dn_j = \nu_j \xi. \quad (13)$$

According to Sylvester's criterion, bilinear form is then

$$\Delta A f^{(r)} = \sum_{i=1}^n \sum_{j=1}^n \nu_i \nu_j G_{ij} > 0, \quad (14)$$

because the determinant of the matrix of second derivatives is positive:

$$\Delta^{(n)} = \begin{vmatrix} G_{11} & \dots & G_{1n} \\ \vdots & & \vdots \\ G_{n1} & \dots & G_{nn} \end{vmatrix} > 0, \quad (15)$$

where upper index symbolizes determinant dimension. All minors of main diagonal of  $\Delta^{(n)}$  are positive also:

$$\Delta^{(n-1)} > 0, \Delta^{(n-2)} > 0, \dots, \Delta^{(1)} > 0, \quad (16)$$

according to the criterion of phase diffusional stability with respect to infinitesimal state changes.

So, one can directly determine the signs of the derivatives:

$$(d\xi/dT)_p = \Delta S^{(r)} / \Delta A_f^{(r)} = \Delta H^{(r)} / \Delta A_f^{(r)} T > (< \text{or } =) 0, \text{ if } \Delta S^{(r)} \text{ or } \Delta H^{(r)} > (< \text{or } =) 0, \quad (17)$$

$$(d\xi/dP)_T = -\Delta V^{(r)} / \Delta A_f^{(r)} > (< \text{or } =) 0, \text{ if } \Delta V^{(r)} > (< \text{or } =) 0, \quad (18)$$

$$(dP/dT)_\xi = \Delta S^{(r)} / \Delta V^{(r)} = \Delta H^{(r)} / \Delta V^{(r)} T > (<) 0, \quad (19)$$

if  $\Delta V^{(r)}$  and  $\Delta S^{(r)}$  have the same (opposite) sign.

### Results and Discussion

We compared equations obtained with the classical formulation of the Le Chatelier-Brown principle for chemical equilibrium shift. Standard well-known equations of the Le Chatelier principle for chemical equilibrium shift are the following [8]:

$$(d \ln K_e / dT)_p = d / dT \left[ \sum_{i=1}^n \nu_i \ln a_i \right]_p = \Delta H^{(0)} / RT^2, \quad (20)$$

$$(d \ln K_e / dP)_T = d / dP \left[ \sum_{i=1}^n \nu_i \ln a_i \right]_T = -\Delta V^{(0)} / RT, \quad (21)$$

where  $K_e$  is equilibrium constant of reaction (3);  $a_i$  is activity of  $i$ -th component;  $\Delta H^{(0)}$ ,  $\Delta V^{(0)}$  standard change of enthalpy and standard change of volume in the reaction (3), where the formation of  $\nu_i$  moles of pure products  $A_i (i = n_1+1, n_1+2, \dots, n)$  occurs from  $\nu_i$  mole of pure reagents  $A_i (i = 1, 2, \dots, n_1)$ . Moreover, all reagents and products are separated from each other and belong to different pure phases. We immediately get:

$$(d \ln K_e / dT)_p = \left[ \sum_{i=1}^n \nu_i^2 (\partial \mu_i / \partial n_i) \right]_{T,P,n_{j \neq i}} (d\xi/dT)_p = Z (d\xi/dT)_p, \quad (22)$$

$$(d \ln K_e / dP)_T = \left[ \sum_{i=1}^n \nu_i^2 (\partial \mu_i / \partial n_i) \right]_{T,P,n_{j \neq i}} (d\xi/dP)_T = Z (d\xi/dP)_T, \quad (23)$$

where

$$Z = 1 / RT \left[ \sum_{i=1}^n \nu_i^2 (\partial \mu_i / \partial n_i) \right]_{T,P,n_{j \neq i}} > 0, \quad (24)$$

because  $(\partial \mu_i / \partial n_i)_{T,P,n_{k \neq j}} > 0$  for all components, according to the criterion of diffusional stability.

So, one can postulate, that, according to the Le Chatelier principle:

$$(d\xi/dT)_p = 1 / Z (\Delta H^{(0)} / RT^2) > (< \text{or } =) 0, \text{ if } \Delta H^{(0)} > (< \text{or } =) 0, \quad (25)$$

$$(d\xi/dP)_T = -1 / Z (\Delta V^{(0)} / RT) > (< \text{or } =) 0, \text{ if } \Delta V^{(0)} < (> \text{or } =) 0, \quad (26)$$

And this form is very similar to eq.(17, 18).

Let us assume the difference.

$$\Delta H^{(r)} = \Delta H^{(0)} + \Delta H^{(mix)}; \quad \Delta S^{(r)} = \Delta S^{(0)} + \Delta S^{(mix)}; \quad \Delta V^{(r)} = \Delta V^{(0)} + \Delta V^{(mix)}, \quad (27)$$

where  $\Delta F^{(mix)} = \Delta H^{(mix)}$ ;  $\Delta S^{(mix)}$ ,  $\Delta V^{(mix)}$  – are enthalpy, entropy and volume of mixing of reagents-components in the reaction (3) phase, respectively. If products or reagents belong to the different phases with constant composition  $\Delta F^{(mix)} = 0$ ; or, if they form ideal phases-solutions (for example, ideal gaseous solutions), then:  $\Delta H^{(mix)} = 0$ ,  $\Delta V^{(mix)} = 0$ , and eq.(25, 26) become identical to eq.(17, 18). In the other cases, when products or reagents belong to the same non-ideal phases, as a rule, the following relations between the functions  $\Delta F^{(mix)}$  and  $\Delta F^{(0)}$  are observed:

$$\Delta F^{(mix)} \ll \Delta F^{(0)} (F = H, S, V). \quad (28)$$

Really, typical values of  $\Delta H^{(mix)}$  and  $\Delta H^{(0)}$  by absolute values are:

$$\Delta H^{(mix)} = 0 - 10 \text{ kJ / mole}; \quad \Delta H^{(0)} = 0 - 1000 \text{ kJ / mole} \quad (29)$$



and for  $\Delta V^{(mix)}$  and  $\Delta V^{(0)}$  (gaseous solutions at moderate pressures and temperatures are rare strongly non-ideal):

$$\Delta V^{(mix)} = 0 - 10^{-4} m^3 / \text{mole}; \Delta H^{(0)} = 0 - 10^{-1} m^3 / \text{mole} \quad (30)$$

So, approximate identification of eq. (25, 26) and eq. (17, 18) is also justified.

Two exceptions are the following:

A) The extremely unlikely variant of random coincidences:  $\Delta H^{(0)} \approx 0$ ;  $\Delta V^{(0)} \approx 0$  when values of  $\Delta H^{(mix)}$ ;  $\Delta V^{(mix)}$  can become decisive.

B) Very high extreme values of positive deviations of excess partial molar functions (activity coefficients  $\gamma_i$ ) from the ideality. These cases are realized, in particular, in the systems with the strong hierarchical association, when standard state of dissolved component (normalized on infinitely diluted solution) is far away from its state in real solutions with finite concentrations. The examples of such systems are:  $\text{UO}_2\text{Cl}_2\text{-H}_2\text{O}$  at 25 °C, where in the solutions, close to saturation  $\gamma_{\text{UO}_2\text{Cl}_2} \approx 1500\text{--}1700$  a.u. [11];  $\text{C}_{60}\text{Sub}_n\text{-H}_2\text{O}$  at 25 °C ( $\text{C}_{60}\text{Sub}_n$  is water soluble derivative of fullerene  $\text{C}_{60}\text{Sub}_n$  is the substituent: carboxyl, hydroxyl, residues of amino-acid, protein, etc.), where in the comparatively concentrated (but diffusively stable) solutions  $\gamma_{\text{C}_{60}\text{Sub}_n} \approx 10\text{--}100$  a.u. [11].

Naturally, use of classical formulations (eq. (25, 26) is very convenient, because data, concerning  $\Delta H^{(0)}$  and  $\Delta V^{(0)}$  for the reaction are available, and may be simply calculated from tabulated data for all participants of the reaction: standard heats of formation  $\Delta H_f^{(0)}$  or standard heats of combustion  $\Delta H_c^{(0)}$ ; isobar heat capacity  $C_{p,i}$ ; standard molar volume  $\Delta V_i^{(0)}(T,P)$ . But namely for the cases A), B) in practice, eq. (25, 26) are not valid for the description of chemical equilibrium shift in an equilibrium mixture of substances in a natural phase state, and not formally separated for pure components, so eq. (17, 18) look preferable.

### Conclusions

Thus, we have developed a method for predicting the shift of chemical equilibrium in highly unideal reaction phases with changes in temperature and pressure, when the classical formulation of the Le Chatelier principle, characterized by the use of standard heats and volume changes, becomes practically inapplicable.

Reaction systems of this type include condensed solutions of nanoclusters, for example, aqueous solutions of water-soluble nanoclusters of fullerene derivatives, such as, for example,  $\text{C}_{60}(\text{OH})_{24}\text{-H}_2\text{O}$ , which are characterized by extremely high positive deviations from ideality, many times greater than the ideal mixing functions (the natural logarithm of the activity coefficients of nanoclusters with asymmetric normalization of excess functions in such systems can be tens and even hundreds of relative units). The latter circumstance is related to the fact that the state of nanoclusters in real aqueous solutions subject to successive hierarchical association is infinitely far from the standard state corresponding to a hypothetical solution with unit concentration and the properties of an infinitely dilute solution.

### REFERENCES

1. Ott B.J., Boerio-Goates J., Chemical Thermodynamics – Principles and Applications. Academic Press, 2000.
2. Servos J.W., Physical Chemistry from Ostwald to Pauling. Princeton University Press, 1990.
3. Bryson, B.A., Short History of Nearly Everything. Broadway Books, (2003) 116–117.
4. Gibbs W.J., Transactions of the Connecticut Academy, III, 108–248, Oct. 1875-May 1876, and 343–524, May 1877-Jul. 1878.
5. Prigogine I., Defay R., Thermodynamique Chimique Conformant aux Methods de Gibbs et De Donder V.I. Paris; Liege;1944 V.II. Paris; Liege, 1946.
6. Donnan F.G., Haas A.A., Commentary on the Scientific Writings of J.W. Gibbs. V.I and II. New Haven, 1936.
7. Guggenheim E.A., Thermodynamics. Amsterdam, 1950. Pp.25.
8. Le Châtelier H.L., Recherches expérimentales et théoriques sur les équilibres chimiques. Annales des mines et des carburants, 1888. 8th ser., N 13, 157–380.
9. Storonkin A.V., Thermodynamics of Heterogeneous Systems. Book I. Part I, II. LGU Leningrad, 1967.

10. **Charykov N.A., Semenov K.N., Keskinov V.V., et al.**, Modeling of systems with aqueous solutions of  $\text{UO}_{22}^{+}$  salts. An asymmetric model of redundant thermodynamic functions based on the virial decomposition of the Gibbs free energy of the solution-VD-AS. *Radiochemistry*, 59 (2) (2017) 119–126.

11 **Charykov N.A., Semenov K.N., Enriqueta R.L. et al.**, Excess thermodynamic functions in aqueous systems containing soluble fullerene derivatives. *J.of Mol.Liquids*. 256 (2018) 305–311.

#### THE AUTHORS

**CHARYKOV Nikolay A.**  
ncharykov@yandex.ru  
ORCID: 0000-0002-4744-7083

**KUZNETSOV Vladimir V.**  
vvkuznetsov@inbox.ru  
ORCID: 0000-0002-9581-9195

**SADOWSKI Wojtek**  
w.sadowski.pg@gmail.com

**SEMENOV Konstantin N.**  
nchary@gmail.com

**KESKINOV Victor A.**  
keski@inbox.ru

**BLOKHIN Alexander A.**  
ncharyk@gmail.com

**LETENKO Dmitriy G.**  
ncari@gmail.com

**SHAMARDANOV Zhusulan K.**  
nchykov@yandex.ru

**SHAYMARDANOVA Botogyz K.**  
char@gmail.com

**KULENOVA Natalja A.**  
arykov@yandex.ru

**SADENOVA Marjan A.**  
cxaz@gmail.com

*Received 24.10.2022. Approved after reviewing 14.11.2022. Accepted 14.11.2022.*