ON THE HISTORY AND RECENT APPLICATIONS OF HYPERFREE ENERGY DESCRIBING THERMODYNAMICS OF MOBILE COMPONENTS IN PARTLY OPEN CERAMIC SYSTEMS

In memory of D.S. Korzhinskiy and P. Holba

#DAVID SEDMIDUBSKÝ*, JAROSLAV ŠESTÁK**

*Department of Inorganic Chemistry, University of Chemistry and Technology,
Technická 5, 166 28 Prague, Czech Republic
**New Technologies - Research Centre of the Westbohemian Region, University of West Bohemia in Pilsen (NTC-ZČU),
Universitní 8, 30114 Pilsen, Czech Republic

#E-mail: sedmidub@vscht.cz

Nonstoichiometric oxides form a new chapter in tailored materials. Founding and construction of thermodynamic functions related to solid (geologic) materials is traced showing interactions between Czech Professor F. Wald and Russians R.S. Kurnakov and D.S. Korzhinskiy in the early definition of phases and characterization of partly open systems. Development of thermodynamic concepts regarding solid-state description is reviewed. For the associated definition of a mobile component the hyperfree energy was invented and recently applied on several systems. A novel term plutability is put forward as a measure of material susceptibility towards free component uptake as a result of varying predictors such as temperature, pressure and activity. Ehrenfest-like equations involving the changes of plutabilities were derived.

INTRODUCTION

While tailoring new materials the scientists often face new thermodynamic predicaments. The recently emerging subject of oxides with variable stoichiometry including their phase equilibria with environment affected the novel field of thermodynamics of nonstoichiometric solids. This field has been promoted by Czech studies, the typical cases of which are represented by either spinels [1, 2], superconductors [3-6], magnetoresistance manganites [7, 8] or thermoelectric cobaltites [9-11] which required a novel approach for treating the interaction between a ceramic material and atmospheric oxygen. It is worth noting that the core of the associated innovative thermodynamic approach was laid by Czech chemist Pavel Holba [12-16] as a continuation of the respected Czech thermodynamic school commenced by Šatava [17, 18] whose international impact is worth of a more detailed analysis.

Historical roots

As it is well known J.W. Gibbs introduced (1876-1878) an important concept of component, chemical potential and phase and ingeniously declared the phase rule [19] famous with dictum "the whole is simpler that its parts" [20]. However, this remarkable inventiveness can be traced back to some Czech-Russian reflections relating the concepts of phase, compound and solution since it was first offered by the Czech chemist F. Wald (1861-1930). In particular Wald´s consideration [21, 22] led in 1912 Russian R.S. Kurnakov (1860-1941) [23] to publish a definition in which so far traditional compounds were distinguished as daltonides while nonstoichiometric compounds were called berthollides [23-25]. This novel idea was continued via detailed examination of nonstoichimetric oxides by Yu.D. Tretyakov (1931-2012) [26]. It is interesting that Kurnakov's student (and co-author of the article, in which berthollide name was first used [24]) was A. I. Glazunov (1888-1951), who after World War I immigrated to Czechoslovakia, where he became the rector of the Czecho-Slovak Mining Academy (founded 1849 in the city Příbram).

Efforts to improve iron and steel products connected with studies of phase composition of metallic samples found an important support in theory of phase diagrams developed by H.E. Roozeboom (1854-1907) who applied Gibbs phase rule to alloys (1900) [27] writing a fundamental book on phase equilibria [28]. The remarkable Lewis' important concept of „activity"

Dedicated to Pavel Holba (1940-2016) one of the outstanding members of the Czech thermodynamic school who specialized on solid-state and its description in relation to heterogeneous solid-gas equilibria.

(1907) [29] brought a more practical form of chemical strength of component and practical depiction of „negative common logarithm of H$^+$ activity" suggested by Sørensen two years later (1909) [30] today's known as *pH* quantity. In 1923 the subsequent development of thermodynamics was accomplished by Lewis new book [31].

In 1936 Korzhinskiy differentiates two classes of components in geochemical systems [32]: inert components whose amounts (masses or numbers of moles) are independent of the amounts of any other component and of the processes inside the system, and perfectly mobile components, whose chemical potentials (or other intensive parameters) are independent factors of equilibrium. All these concepts had formed a basis for a number of studies of real material systems in chemistry, geochemistry, metallurgy, hydrochemistry and material science. Another attempt to overcome the traditional limits of closed systems was accomplished by Ellingham in 1944 [33] showing the relationships between decomposition temperatures of various metal oxides in terms of ΔG vs T plot. In 1948, Richardson & Jeffes [34] improved Ellingham diagrams by adding a monographic scale, which allowed reading the decomposition temperature of metal oxide under various types of atmosphere formed by gaseous mixtures (such as O_2 + inert gas, $CO + CO_2$ and/or $H_2 + H_2O$). It seems that the so called „Richardson diagrams" appeared three years after the foremost publication by Darken & Gurry [35] on the equilibrium non-stoichiometry of wüstite dealing with equilibria of condensed Fe-O phases under the controlled gaseous atmosphere (captivatingly prepared by using a new gas-mixing technique). A notable result in this direction was the significant book by Muan & Osborn [36], which presented phase diagrams obtained under conditions of partly open systems, e.g., under air atmosphere or in the contact with liquid iron. Another application, overcoming the standard concept of closed systems was established by Pourbaix in 1946 [37], who suggested the diagrams consisting of the plot of redox potential (*E*) versus acid-base potential (*pH*) to portray equilibria of dilute aqueous solution at room temperature. Associated applications became widely known in hydrochemistry probably due to books by Garrels [38] and Garrels & Christ [39]. Apart from the above mentioned English-written books, Korzhinskiy also helped to develop a physicochemical basis for the analysis of mineral parageneses revealing it in 1957 Russian book [40] translated into English in 1959 [41]. In this book Korzhinskiy also presented his concept of new thermodynamic potentials for systems with wholly mobile components developed one decade before [42,43]. Nevertheless, the application of his new potentials was first rejected by geologist Nikolayev [44], however, publications of Verhoogen [45] and Thompson [46] as well as the paper by Palatnik & Landau [47,48] supported Korzhinskiy in his thoughts. Later in 1956

Korzhinskiy published a derivation of thermodynamic potentials for systems with mobile components in a more internationally available Russian journal [49].

It seems to be evident that during the last half of century no information on Korzhinskiy's systems considering mobile components was proficient to infiltrate from the world of geologists into the world of chemists counting the Russian books by Bulach [50], Tretyakov [26, 52] and the Czech textbook [17] where the former one [50] included a particular chapter „Phase diagrams for open systems". In 1970s the study of equilibria of oxides with atmosphere was also stimulated by the industry's interest in the production of new ceramic materials (e.g., ferrites [1, 26]) of required properties using an adequate high-temperature preparation procedure. Consequently, a new thermodynamic school developed in cooperation between the Czech Institute of Physics and the University of Chemistry and Technology (former Institutre of Chemical Technology) hindered at that time by political repressions [53] revealed in 1990´s [14-16] and successively continued through the studies of oxide high-temperature superconductors [3-7] and followed by others (e.g. most recently cobaltites [9-11] prominent for their thermoelectric properties). However, in spite of so much work, which was concentrated on these systems of variable solid-gas interaction [1-11] no adequate thermodynamic resolution towards the partly open systems became accessible so that the case of related hyperfree energy is worth of more detailed presentation.

Definition of partly open systems and the concept of hyperfree energy

Long lasting experience with nonstoichiometric materials has looked-for a new terminology such as that for partly open systems containing both the free components (capable of exchanging between the system and its surroundings) and conservative components (whose amounts are remaining constant). In fact, we can observe plenty of systems whose components (e.g., water, oxygen, CO_2) are exchanged with (i.e., can escape into or be absorbed from) the surroundings but other components remain unchanged in the system under consideration.

Conditions necessary for the system isolation from its surroundings with respect to the exchanging components can be labeled in analogy to the standard pairs: adiabatic-isothermal and isochoric-isobaric. A new pair would become [54]: isopletic-isodynamic when plethos (πλήθος) denotes the Greek amount and dynamis (δύναμεις) means a power, strength or ability. Using the last mentioned terms the classification of *N*-component systems can be introduced, where two different types of components, i.e., *c* – conservative (permanent) components and *f* – free (mobile) components can be comprehended. The *N*-component system with N_f free

components and $N_c = (N - N_f)$ conservative components can be identified as a quasi-N_c-component system, e.g., a system of three components consisting of one free component can be called „quasibinary system". For the thermodynamic analysis of such partly open systems it is appropriate to express the composition in terms of *quasimolar fractions* Y_i defined as

$$Y_i = N_i/\Sigma_c N_c = X_i / (1 - \Sigma_f X_f) \qquad (1)$$

On continuing we can say that it was Pavel Holba (1940-2016) [53-62] who implemented an innovative thermodynamic potential for partly open systems rediscovering and properly applying the correct meaning of hyperfree energy Z. It is defined as a Legendre transformation of the standard Gibbs free energy, G, with respect to a free component amount

$$Z = G - N_f \mu_f$$
via specification $Z = f(T, p, \{N_c\}, \{\mu_f\})$ $\qquad (2)$

where N_f is the molar content of free component f in the system and μ_f is its chemical potential. Since the free component f is supposed to be shared with the surrounding atmosphere serving as a reservoir, its chemical potential in the condensed system is equal to its chemical potential in the surroundings and is given as a sum of the standard chemical potential and the logarithmic term involving activity ($\mu_f = G_f^\circ + RT \ln a_f$). Worth noting again is the primary Korzhinskiy´s idea [43,49] to distinguish between the mobile (free) components (shared with the surroundings) and the inert (conservative) components whose pioneering thermodynamic potentials were used in physical geochemistry, but unfortunately did not penetrated to the textbooks of solid-state chemical thermodynamics. This approach is valuable for the thermodynamic description of all systems involving the interaction with the surroundings commonly studied by methods of thermal analysis [58].

The associated hyperfree energy became useful for the construction of crystal-chemical models allowing to estimate the relations between, e.g., the amount of crystal point defects and the equilibrium content of free component [54, 61] as well as for the description of equilibrium behavior of nonstoichiometric phases [36, 53-62]. The thermodynamic treatment is quite analogous to that used for closed systems except that the Gibbs energy is replaced by hyperfree energy in the corresponding equations describing the equilibrium conditions. For instance, the phase transitions between the phases that are stoichiometric with respect to inert components but differ in free component content can be simply described considering the condition of equality of hyperfree energies at the point of phase transition, $\Delta Z = 0$. Similarly, the composition Y_{sol} of a phase revealing a miscibility between inert components and coexisting with a stoichiometric phase of composition Y_{st} can be found by minimizing the thermodynamic potential with respect to Y_{sol}, yielding well known relation:

$$\frac{\partial Z_{sol}}{\partial Y_{sol}} = \frac{Z_{sol} - Z_{st}}{Y_{sol} - Y_{st}} \qquad (3)$$

Moreover, for phases with variable content of free component the hyperfree energy has to be minimized with respect to non-stoichiometry parameter resulting in an equilibrium condition

$$\left(\frac{\partial Z}{\partial \delta}\right) = \Delta G_{If}^\circ + RT \ln K(\delta, a_f) = 0 \qquad (4)$$

describing the incorporation of free component from the surroundings into the given phase.

The concept described above was further extended by deriving the related Clapeyron-like and Ehrenfest-like equations for partly open systems describing the mutual variations of predictor quantities (e.g. T-a_f, p-a_f, a_f-a_g) on the boundaries between the individual phase fields providing thus a versatile tool for the construction of the corresponding potential phase diagrams. In general, one can distinguish between sharp and partial phase transitions when crossing the phase fields borderlines in this type of phase diagrams, which can be associated, respectively, with the first and second order phase transitions within the original Ehrenfest classification scheme. It should be noted, however, that the latter ones should not be confused with the critical (or lambda) phase transition described by Landau. The sharp transitions taking place in the space of variables involving the activity of free components are accompanied by abrupt changes of their contents, ΔY_f. Hence, although the change of hyperfree energy, $\Delta Z_{\varphi-\psi}$ is zero at the borderline between phase fields φ and ψ, its derivatives with respect to free component activities, $(\Delta Z_{\varphi-\psi}//\ln a_f)_{T,p} = \Delta Y_f$, are nonzero and we can apply the same approach as that used to derive the Clapeyron equation, yielding, for instance

$$\left(\frac{d \ln a_f}{d(1/T)}\right)_p = -\frac{[\partial(\Delta Z/T) / \partial(1/T)]_{a_f, p}}{\left(\frac{\partial(\Delta Z/T)}{\partial} \ln a_f\right)_{T, p}} = \frac{\Delta H}{R \Delta Y_f} \qquad (5)$$

$$\left(\frac{d \ln a_f}{d \ln a_g}\right)_{p, T} = -\frac{[\partial(\Delta Z/T) / \partial \ln a_g]_{p, T, a_f}}{[\partial(\Delta Z/T) / \partial \ln a_f]_{p, T, a_g}} = \frac{\Delta Y_g}{\Delta Y_f} \qquad (6)$$

A more complicated situation is encountered if we are dealing with partial transitions characterized by an onset of precipitation of a new phase, where $\Delta Y_f = 0$, however, since Y_f is a continuous but not smooth function of predictors on the borderline delimiting the partial transition, its derivatives undergo abrupt changes. In this line of attack Holba challenged to coin new specialized quantities [55, 57] defining the variation of free component composition with respect to the predictor variables T, p, a_f, a_g. In analogy to the nomenclature used for analogous quantities such as isothermal compressibility or heat capacity he proposed a new term *plutability* (derived from Greek πλούτος = rich, hence the susceptibility to enrichment by a given component).

Based on this definition we can obtain:

$$\kappa_{ff} = (Y_f / \ln a_f)_{T,p}$$
$$\kappa_{fT} = (Y_f / \ln T)_{af,p} \qquad (7)$$
$$\kappa_{fp} = (Y_f / \ln p)_{af,T}$$

denoted as proper plutability, thermal plutability and pressure plutability, respectively.

Following the approach of Ehrenfest, we can apply the l'Hospital rule on the indefinite forms resulting from Equations (5) and (6) and derive Ehrenfest-like equations involving the changes of plutabilities and other quantities that represent the second derivatives of the thermodynamic potential (ΔC_p, $\Delta \alpha$, $\Delta \beta$ standing for heat capacity, thermal expansion and compressibility changes)

$$\left(\frac{\partial \ln a_f}{\partial (1/T)} \right)_P = \frac{\Delta C_p}{R \, \Delta \kappa_{fT}} = \frac{TV \Delta \alpha}{R \, \Delta \kappa_{fP}} = \frac{TV^2 \, \Delta \kappa_{fT}}{\Delta \kappa_{ff}} \qquad (8)$$

$$\left(\frac{\partial \ln a_f}{\partial \ln a_g} \right)_{p,T} = -\frac{\Delta \kappa_{gT}}{\Delta \kappa_{fT}} = -\frac{\Delta \kappa_{gp}}{\Delta \kappa_{fp}} = -\frac{\Delta \kappa_{gf}}{\Delta \kappa_{ff}} = -\frac{\Delta \kappa_{gg}}{\Delta \kappa_{fg}} \qquad (9)$$

Practical application – construction of potential phase diagrams

Let us demonstrate the application of the derived equations on the example of Ca–Co–O system [25] presented in Figure 1. The phase equilibria in such three-component system with a single free component (O) can be represented in a quasibinary (isoactivity section) phase diagram shown in Figure 1b which exhibits exactly the same topological characteristics as conventional binary phase diagrams of closed systems. Conversely, if we fix the cation composition and release the free component activity, we get an isoplethal $T – \log a_f$ section presented in Figure 1a, for which Equations

(5) and (8) can be applied. The upper two transitions, $(Ca_3Co_2O_6 + Ca_3Co_{3.9+x}O_{9.3-\delta}) \rightarrow (Ca_3Co_2O_6 + Ca_{1-x}Co_xO)$ and $(Ca_3Co_2O_6 + Ca_{1-x}Co_xO) \rightarrow Ca_{1-x}Co_xO$ (#1+#2), are typical sharp transitions where the Clapyeron-like equation (5) is applicable. Note that if ΔY_O is constant such as in the latter case, the corresponding borderline must by linear in $(1/T)$ representation and hyperbolic in T representation, see Figure 1.

By contrast, the lower lying borderline represents a partial phase transition between the solution phase $Ca_3Co_{3.9+x}O_{9.3-\delta}$ (misfit phase, MF) and the two-phase region of this phase and $Ca_3Co_2O_6$ (columnar phase, C) whose content is vanishing when crossing the boundary. Hence the first Ehrenfest-like equation (8) must be used. Clearly both ΔY_O and ΔH are zero at the transition, since the phase fraction of MF $\xi = 1$ within the single phase region and it starts to decrease at the borderline. Hence, differentiating

$$\Delta Y_O = (\xi - 1) \, Y_O + (1 - \xi)(6/5) = 0 \qquad (10)$$

with respect to T and $\ln p_O$ we obtain

$$\Delta \kappa_{OT} = (\xi - 1) \kappa_{OT} + \left(Y_O - \frac{6}{5} \right) \left(\frac{\partial \xi}{\partial T} \right)_{p,T} = \left(Y_O - \frac{6}{5} \right) \left(\frac{\partial \xi}{\partial T} \right)_{p,p_O} \qquad (11)$$

$$\Delta \kappa_{OT} = (\xi - 1) \kappa_{OO} + \left(Y_O - \frac{6}{5} \right) \left(\frac{\partial \xi}{\partial \ln p_O} \right)_{p,T} =$$

$$= \left(Y_O - \frac{6}{5} \right) \left(\frac{\partial \xi}{\partial \ln p_O} \right)_{p,T} \qquad (12)$$

and

$$\frac{\Delta \kappa_{OT}}{\Delta \kappa_{OO}} = \frac{(\partial \xi / \partial T)_{p,p_O}}{(\partial \xi / \partial \ln p_O)_{p,T}} \qquad (13)$$

It is noteworthy that the latter quantity occurring in Equation (8) depends neither on Y_O nor on κ_{OT} (and κ_{OO}) which are all canceled in the resulting fraction, but
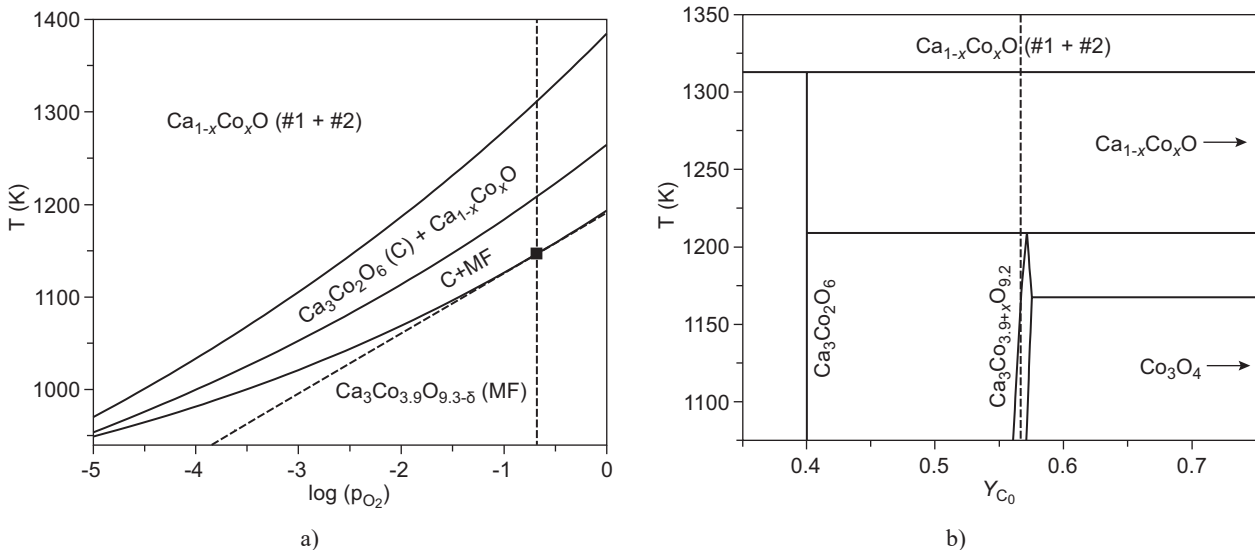

a)

b)

Figure 1. a) T vs. $\log p_{O_2}$ phase diagram of Ca–Co–O system for Ca : Co = 3 : 3.9 (dashed line – isoactivity section shown in b); b) T vs. Y_{Co} isoactivity section ($p_{O_2} = 0.21$) of Ca–Co–O phase diagram (dashed line – isoplethal section shown in a).

only on the slopes of ξ at the phase boundary. Second, the borderline should be linear in T provided the $\Delta\kappa_{OT}/\Delta\kappa_{OO}$ ratio was constant, which is apparently not the case as seen from Figure 1a; the dotted line corresponds to the integrated Equation (8) with this ratio taken constant, $\Delta\kappa_{OO}/\Delta\kappa_{OT} = 28$ K, as obtained for $p_{O_2} = 0.21$ and the respective transition temperature $T_t = 1148$ K. Third, both $\Delta\kappa_{OT}$ and $\Delta\kappa_{OO}$ are accessible from experiment. However, while $\Delta\kappa_{OT}$ can be directly evaluated from TGA data recorded at constant p_{O2}, $\Delta\kappa_{OO}$ requires more sophisticated equipment (TGA with controlled variable p_{O2} or a coulometric titration). If $\Delta\kappa_{OO}$ is not available one can take use of another relation resulting from Equation (8), namely

$$\frac{\Delta\kappa_{OT}}{\Delta\kappa_{OO}} = \frac{\Delta C_p}{RT^2\,\Delta\kappa_{OT}} = \frac{H(\text{MF}) - H(\text{C})}{RT^2\,(Y_O - {}^6\!/_5)} - \frac{H^{\circ}_O}{RT^2} \quad (14)$$

requiring the knowledge of enthalpies of both involved phases and gaseous oxygen at the transition temperature. This example should demonstrate how the presented equations can be applied for the construction of potential phase diagrams from experimental data or for the assessment of thermodynamic quantities necessary for the theoretical calculation of phase equilibria.

Conclusively, as of the four new Clapeyron-like Equations (5), (6) and two additional (involving pressure) P. Holba derived as many as twenty eight such pioneering Ehrenfestian equations published in his last communication [61] completed just few days before his death. It is great pity that such a gifted thermodynamist could not carry on publishing his concepts yet additionally in the form of a regular paper.

CONCLUSION

The hyperfee energy and a new class of Clapeyronian and Ehrenfestian equations can be found useful for the equilibrium studies and construction of thermodynamic models of nonstoichiometric phases [54-57] as well as for the construction of simple phase diagrams reflecting the equilibrium phase relations under a given controlled atmosphere [54, 58, 61]. The impact of Pavel Holba to better understanding thermodynamic background of processes [18] and his encouragement of novel thermodynamic description of partly open system [15, 16] is drawn to a wider attention laying emphasis on the fact that he was one of the followers of the renowned Šatava´s Czech thermodynamic school [16-18, 22, 61] somehow instigated in the early issues of the journal Silikaty [18]. Holba´s noteworthy legacy prominent within Russian circles [62] was the motivation for his awarding by the prestigious Kurnakov medal in thermodynamics conferred in memoriam during the XV International Conference on Thermal Analysis held in Saint Petersburg 2016.

Acknowledgement

REFERENCES

1. Holba P., Khilla M.A., Krupička S. (1973): On the miscibility gap of spinels $Mn_xFe_{3-x}O_4$. *Journal of Physics and Chemistry of Solids*, *34*(3), 387-95. (later transferred to the Phase Diagrams for Ceramists, Vol. 4) doi: 10.1016/0022-3697(73)90030-9

2. Nádherný L., Jankovský O., Sofer Z., Leitner J., Martin Ch., Sedmidubský D. (2015): Phase equilibria in the Zn–Mn–O Spinel system. *Journal of the European Ceramic Society*, *35*, 555-560. doi: 10.1016/j.jeurceramsoc.2014.09.008

3. Šesták J., Moiseev G.K., Holba P., Tsagareishvili D.S. (1994): Oxide-Phase Simulated Thermodynamics of Compounds Auxiliary to $YBa_2Cu_3O_{7+\delta}$ Superconductors. *Japanese Journal of Applied Physics*, *33*, 97-102. doi:10.1143/JJAP.33.97

4. Nevřiva M., Kraus H., Sedmidubský D. (1996): Phase Equilibria Study in the Partially Open Cu–(O) and Me––Cu–(O) (Me=Sr,Bi,Ba) Systems. *Thermochimica Acta*, *282-283*, 205-224. doi: 10.1016/0040-6031(95)02817-X

5. Šesták J., Sedmidubský D., Moiseev G. K. (1997): Some Thermodynamic Aspects of High Temperature Superconductor. *Journal of Thermal Analysis*, *48*, 1105-1122. doi:10.1007/BF01979157

6. Sedmidubský D., Leitner J., Knížek K., Strejc A., Nevřiva M. (2000): Phase Relations in Hg–Ba–Ca–Cu–O System. *Physica C: Superconductivity*, *341-348*, 509-510. doi: 10.1016/S0921-4534(00)00566-9

7. Sedmidubský D., Strejc A., Nevřiva M., Leitner J., Martin Ch. (2003): Structural and Phase Relations in the Sr–Mn–O System. *Solid State Phenomena*, *90-91*, 427-432. doi: 10.4028/www.scientific.net/SSP.90-91.427

8. Sedmidubský D., Nevřiva M., Leitner J., Strejc A., (2006): Single Crystal Growth of $Bi_{1-x}Sr_xMnO_3$ – Thermodynamics and Experiment. *Thermochimica Acta*, *450*, 38-41. doi: 10.1016/j.tca.2006.07.015

9. Jankovský O., Sedmidubský D., Rubešová K., Sofer Z., Leitner J., Růžička K., Svoboda P. (2014): Structure, oxygen non-stoichiometry and thermal properties of $Bi_{1.85}Sr_2Co_{1.85}O_{7.7-\delta}$ ceramics. *Thermochimica Acta*, *582*, 40-45. doi:10.1016/j.tca.2014.12.002

10. Jankovský O., Sedmidubský D., Sofer Z., Šimek P., Hejtmánek J. (2012): Thermodynamic behavior of $Ca_3Co_{3.93+x}O_{9+\delta}$ ceramics. *Ceramics – Silikáty*, *56*, 139-144.

11. Jankovský O., Sedmidubský D., Sofer Z., Čapek J., Růžička K. (2013): Thermal Properties and homogeneity range of $Bi_{24+x}Co_{2-x}O_{39}$ ceramics. *Ceramics-Silikáty*, *57*, 83-86.

12. Holba P. (1972): On calculations of activities of chemical individuals from disorder models. *Thermochim Acta, 3,* 475. doi:10.1016/0040-6031(72)85007-X

13. Holba P. (1976): Thermodynamic aspects of thermal analysis of solids. *Ceramics-Silikáty*, *20*, 45. (in Czech)

14. Holba P., Nevřiva M. (1990): Phase-diagram analysis of oxide systems with reset to the laws of thermodynamics. *Ceramics-Silikáty*, *34*, 77-90.

15. Holba P. (1992): Thermodynamics of partially open systems. *Czechoslovak Journal of Physics*, *42*, 549-575.

16. Holba P. (1994). Thermodynamics and Ceramic Systems, in: Koller A. (Ed.): *Structure and Properties of Ceramic Materials*. Elsevier, Amsterdam/Tokyo. pp. 17-113.

17. Šatava V. (1962): *Introduction to the physical chemistry of silicates*. SNTL, Prague. (in Czech)

18. Holba P., Šesták J. (2012): Czechoslovak footprints in the development of methods of calorimetry and thermal analysis. *Ceramics-Silikáty*, *56*, 159-167.

19. Gibbs J.W. (1876): On the equilibrium of heterogeneous substances. *Tranaction of the Connecticut Academy of Art and Sciences*, *3*, 108-248, 343-524.

20. Proks I. (2012). *Whole is simpler than its parts: The selected chapters from thermodynamic history*. Slovak Academy of Sciences, Bratislava. (in Slovak)

21. Wald F. (1899): Was ist ein chemisches Individuum? *Zeitschrift für Physikalische Chemie*, *28*, 13-16.

22. Wald F. (1918). *Chemie fasí* (Chemistry of phases), Czech Academy of Art, Prague.

23. Kurnakov N.S. (1914): Compound and chemical individual. Izv. Imperator. Akad. Nauk (Bull. Acad. Imp. Sci. de St-Pétersbourgh).

24. Kurnakov N.S., Glazunov A.I. (1912): Alloys of cadmium with silver and copper. *Journal of Russian Physico-Chemical Society*, *44*, 1007.

25. Kurnakov N.S. (1924): Continuousness of chemical transitions of substance. *UFN*, *4*, 339-356.

26. Tretyakov Yu.D. (1967). *Thermodynamics of ferrites*. Izd. Khimia, Leningrad. (in Russian)

27. Bakhuis-Roozeboom H.E. (1900): Eisen und Stahl vom Standpunkte der Phasenlehre. *Zeitschrift für Physikalische Chemie*, *34*, 437-487.

28. Bakhuis-Roozeboom H.E. (1901-1911). *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre Vol. I-III*. Braunschweig,

29. Lewis G.N. (1907): Outline of a New System of Thermodynamic Chemistry. *Proceedings of the American Academy of Arts and Sciences*, *43*, 259–293.

30. Sørensen S.P.L. (1909): Enzym Studies II. on Measurement and Importance of Hydrogen-Ion Concentration at Enzymatic Processes. *Biochemische Zeitschrift*, *8*, 131-200. (in Swedish)

31. Lewis G.N., Randall M. (1923). *Thermodynamics and the Free Energy of Chemical Reactions.* McGraw-Hill.

32. Korzhinskiy D.S. (1936). *Mobility and inertness of components at metamorphosis*. Izv. Akad. Nauk SSSR, Ser. geol. No.1.

33. Ellingham H.J.T. (1944): The physical chemistry of process metallurgy. *Journal of the Society of Chemical Industry*, *63*, 125.

34. Richardson F.D., Jeffes J.H.E. (*1948)*: Free energies of formation of metal oxides as a function of temperature. *Journal of the Iron and Steel Institute*, *160*, 261-273.

35. Darken L.S., Gurry R.W. (*1946)*: The system iron – oxygen *I. , II. Journal of the American Chemical Society*, *67*, 1398-1412; *68*, 798−816.

36. Muan A., Osborn E.F. (1965). *Phase Equilibria Among Oxides in Steelmaking*. Addison-Wesley Reading, MA.

37. Pourbaix M.J.N. (1949). *Thermodynamics of Dilute Aqueous Solutions*. E.Arnold & Co., London (French original: Thermodynamique des Solutions Aqueses Diluées from 1946)

38. Garrels R.M. (1960). *Mineral Equilibria*. New York.

39. Garrels R.M., Christ C.L. (1965). *Solutions, minerals, and equilibria*. Harper & Row, New York.

40. Korzhinskiy D.S. (1957). *Physicochemical basis of the analysis of the paragenesis of minerals*. Izd. Akad. nauk SSSR, Moskva. (in Russian)

41. Korzhinskiy D.S. (1959). *Physicochemical basis of the analysis of the paragenesis of minerals*. Consultants Bureau, New York. (English translation)

42. Korzhinskiy D.S. (1944): Sootnosheniye mezhdu mineralogicheskim sostavom i velichinoy khimicheskich potentsialov komponentov (Relations between mineralogical composition and values of chemical potential of components). *Zap. Vseross. min. obshch.*, *73* [1].

43. Korzhinskiy D.S. (1949): Termodinamicheskiye potentsialy otkrytych sistem i primer ich primeneniya v geokhimii (Thermodynamic Potentials of Open Systems and Example of their Application in Geochemistry). *Izv. Sektora fiz.-khim. analiza Akad. nauk SSSR*, *19*.

44. Nikolayev V.A. (1954): Ob odnom iz osnovnych uravneniy termodinamiki i ego primeneniy k otkrytym sistemam (On one of the Fundamental Equations of Thermodynamics and on its Application to Open Systems). *Zap. Vses. min. obshch.*, *83* [4].

45. Verhoogen J. (1949). *Thermodynamics of a magmatic gas phase*. University of California Press.

46. Thompson J.B. (1955): The thermodynamic basis for the mineral fancies concept. *American Journal of Science*, *253* [2], 65-103.

47. Palatnik L.S., Landau A.I. (1955): K teorii ravnovesia geterogennych mnogokom-ponentnykh sistem (On Theory of Equilibrium of Heterogeneous Multicomponent Systems); *Dokl. Akad. nauk SSSR*, *102* [1], 125.

48. Palatnik L.S., Landau A.I. (1961). *Fazovye ravnovesiya mnogokomponentnykh sistemakh (Phase Equilibria of Multicomponent Systems)*. Izd. Charkov. univ., Charkov.

49. Korzhinskiy D.S. (1956): Vyvod termodinamicheskikh potentsialov sistem s podvizhnymi komponentami (Derivation of Thermodynamic Potentials of Systems with Mobile Components). *Dokl. Akad. nauk SSSR*, *106* [2].

50. Bulach, A.G. (1968). Metody termodinamiki v mineralogii (Methods of Thermodynamics in Mineralogy). Izd. Nedra, Leningrad.

51. Rieder M., Povondra P. (1997). *Fázové rovnováhy pro geology (Phase Equilibria for Geologists)*. Karolinum, Praha.

52. Tretyakov Yu. D. (1974). *Khimia nestekhiometricheskih okislov (Chemistry of Nonstoichiometric Oxides)*. Izd. Mosk.Univ., Moskva.

53. Holba P. (1970). *Equilibria of Mn–Fe–O Spinels with Gaseous Oxygen and Their Interpretation*, Dissertation with 110 pp was forbidden to defending as well as publishing due to political reasons, Prague. (in Czech)

54. Holba P. (2011). New thermodynamic potentials and Clapeyron equations for condensed partly open systems applicable to nonstoichiometric phases, in: Šesták J., Holeček M., Málek J. (Eds.): *Thermodynamic Structural and Behavioral Aspects of Materials Accentuating Non-Crystalline States*. OPS Plzeň-Liberec. pp. 98-115

55. Holba P., Sedmidubský D. (2013): Heat capacity equations for nonstoichiometric solids. *Journal of Thermal Analysis and Calorimetry*, *113*, 239-245. doi:10.1007/s10973-012-2886-1

56. Holba P. (2013). Equilibrium background of processes initiated by heating and Ehrenfests´ classification of phase transitions, in: Šesták J., Šimon P. (Eds.): *Thermal analysis of micro- nano- and non-crystalline materials: Transformation, crystallization, kinetics and thermodynamics.* Springer Berlin. pp. 29-52.

57. Sedmidubský D., Holba P. (2015): Material properties of nonstoichiometric solids. *Journal of Thermal Analysis and Calorimetry*, *120*, 183-188. doi:10.1007/s10973-015-4466-7

58. Holba P. (2015): Ehrenfest equations for calorimetry and dilatometry. *Journal of Thermal Analysis and Calorimetry*, *120*, 175-181. doi:10.1007/s10973-015-4406-6

59. Holba P., Sedmidubský D. (2013). Crystal defects and nonstoichiometry contributions to heat capacity of solids, in: Šesták J., Šimon P. (Eds.): *Thermal analysis of micro- nano- and non-crystalline materials: Transformation, crystallization, kinetics and thermodynamics.* Springer Berlin. pp. 53-74. doi:10.1007/978-90-481-3150-1_3

60. Holba P. (2015): Termodynamický popis tepelných kapacit v nestechiometrických fází (Thermodynamic description of heat capacities of nonstoichiometric phases). *Chemické Listy, 109,* 113–116. (in Czech)

61. Holba P, Sedmidubský D. (2017). Clapeyron and Ehrenfest equations and hyperfree energy for partly open systems, in: Šesták J., Hubík P., Mareš J.J. (Eds.): *Thermal Physics and Thermal Analysis: From macro to micro highlighting thermodynamics, kinetics and nanomaterials*, Springer (in print, ISBN 978-3-319-45897-7).

62. Šesták J., Holba P., Gavrichev K.S. (2015) Reinstatement of thermal analysis tradition in Russia and related East European interactions. *Journal of Thermal Analysis and Calorimetry*, *119*, 779-784. doi:10.1007/s10973-014-4151-2