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On Application of Hyperfree Energy for the Description of Thermodynamics of Mobile Components in Nonstoichiometric Partially Open Ceramic Systems

Jaroslav Šesták

Abstract

Nonstoichiometric oxides form a new chapter in tailored materials. Founding and construction of thermodynamic functions related to solid (geologic, metallurgic) materials is traced showing interactions between Czech Professor F. Wald and Russians R.S. Kurnakov and D.S. Korzhinskiĭ and further developed by Czech P. Holba in the initial phase definition and related characterization of partially open systems. A gradual increase in thermodynamic concepts related to solid-state description is investigated in more detail. For the associated thermodynamic definition of the mobile component, the previously formulated hyperfree energy function, which was recently applied to several systems, was used. As a measure of the material disposition for the absorption of the free component, an innovative term of plutability is proposed, which allows the introduction of various forecaster variables such as temperature, pressure, and activity. Examples of practical application are examples of high-temperature superconducting materials, where the Czech school of thermodynamics is emphasized.

Keywords: stoichiometry, ceramics, hyperfree energy, superconductors, quasimolar, plutability

1. Introduction and historical roots

While preparing a new kind of materials, the scientists often face inquiry of adjusting new thermodynamic predicaments. The recently emerging subject of oxides exhibiting variable stoichiometry is included with associated phase equilibria in relation to its environment. It influenced the new field of thermodynamics of nonstoichiometric solids, whose field was also promoted by Czech studies and whose typical cases may be represented by either spinels [1, 2], superconductors [3–6], magnetoresistance manganites [7, 8] or thermoelectric cobaltites [9–11] and all of which requiring a new approach to treating interactions between ceramic material in solid and atmospheric oxygen. It is worth of taking a notice of the core of the associated innovative thermodynamic approach, was provided by Czech physical chemists Pavel Holba [12–16], as a continuation of the recognized and

previously encouraged Czech school of solid-state thermodynamics launched by Vladimír Šatava (1924–2012) [17, 18], whose worldwide international impact deserves more attention (**Figure 1**).

It was well-known that it was Josiah W. Gibbs (1876–1878), who introduced an important concept of component, chemical potential, and phase along with the ingeniously declared the phase rule [19] famous with dictum, citing: “the whole is simpler than its parts,” which was genially extended in the book by Ivo Proks [20]. However, this remarkable inventiveness can be traced back to some Czech-Russian reflections relating the concepts of phases, compounds, and solutions, as it was first historically introduced by the Czech chemist František A. Wald (1861–1930). In particular, Wald’s consideration [21, 22] led in the year 1912, the Russian R.S. Kurnakov (1860–1941) [23] to develop and publish a definition in which so far customary compounds were distinguished twofold as daltonides and berthollides [23–25], the latter factually being nonstoichiometric compounds. This novel idea was sustained via a more detailed examination of nonstoichiometric oxides by Yu. D. Tretyakov (1931–2012) [26]. It should be noted that Kurnakov’s student and co-author of the article in which the name berthollide was first used [24] was A.I. Glazunov (1888–1951), who after World War I immigrated to former Czechoslovakia. Quaintly, he became the Rector of the Czech-Slovak Mining Academy, which was founded in 1849 in the town of Příbram.

The care for improving iron and steel products associated with various phase-composition studies of metallic samples has found a significant support in phase-diagram theory than that developed by H.E. Roozeboom (1854–1907). He was capable to apply the Gibbs phase rule in the direction of alloys (1900) [27], writing moreover a fundamental book on phase equilibria [28]. The remarkable Lewis’ important concept of “activity” (1907) [29] brought a more practical form of chemical strength toward a component as well as a practical depiction of so-called: “negative common logarithm of H^+ activity” suggested, however, by Sørensen 2 years later (1909) [30] as the today’s known pH quantity. In 1923, the subsequent advancement of improved thermodynamic description was accomplished by Lewis in his new book [31].

Captivatingly, Korzhinskiy in 1936 assumed the differentiation of two classes of components useful in geochemical systems [32]. Thus, they were *inert components*



Figure 1.

The personalities staying behind the development of the so-called Czech thermodynamic school applied to the solid-state. From left: Pavel Holba (1940–2016), Vladimír Šatava (1924–2012) and Jaroslav Šesták (1938–).

whose amounts (e.g., weight or number of moles) remain independent of the amount of any other component and processes within the system, and entirely *mobile components* whose chemical potentials (and/or other intensive parameters) remain independent of equilibrium. All these concepts formed the basis for a series of studies on real material systems in a number of fields of chemistry, geochemistry, metallurgy, hydrochemistry, and material sciences. Further efforts to overcome the traditional limits on fully enclosed systems were made by Ellingham in 1944 [33]. He formed relationships between decomposition temperatures of various metal oxides in the renowned graph ΔG vs. T . In 1948, there were Richardson and Jeffes [34], which improved the traditional Ellingham diagrams by adding a so-called *monographic scale* that allowed reading the decomposition temperature of metal oxide under different types of atmospheres consisting of different gas mixtures such as O_2 + inert gas, CO + CO_2 and/or H_2 + H_2O . It looks like that the so-called “Richardson diagrams” come into sight 3 years after the foremost publication by Darken and Gurry [35, 36], dealing with the nonstoichiometry equilibrium of wüstite describing equilibria for the condensed Fe-O phases under the controlled gaseous atmosphere. Captivatingly, the experimental process by using a new gas-mixing technique was pioneering for new incoming techniques. A remarkable result in this stimulus was an important book by Muan and Osborn [37], which presented phase diagrams obtained under partially open-system conditions, for example, either in the air atmosphere or in contact with liquid iron. A distinctive application that actually surpasses the standard concepts of closed system display was established by Pourbaix in 1946 [38]. He proposed new diagrams consisting of a graph of redox potential (E) versus acid–base potential (pH) to appropriately show the equilibrium of the diluted aqueous solution at room temperatures. The coupled application has become widely known in hydrochemistry most likely due to Garrels [39] and Garrels and Christ [40]. In addition to the above-mentioned English-written books, Korzhinskiĭ has also helped to cultivate a physicochemical basis for the analysis of mineral paragenesis, which was revealed it in 1957 by a Russian book [41] also translated into English in 1959 [42].

Worth noting again is the special Korzhinskiĭ's differentiation of two classes of components in geochemical systems developed as early as in 1936 [14]. It were sorted as *inert components*, whose amounts (such as masses or numbers of moles) are independent of the amounts of any other component as well as of any processes inside the system, and *perfectly mobile components*, whose chemical potentials (or other intensive parameters) are independent factors of equilibrium [43, 44]. Afterward, he was making available the concept of thermodynamic potentials for systems containing entirely mobile components. However, requests for his new potential were first rejected by geologist Nikolaev [45], but Verhoogen [46] and Thompson [47], as well as by Palatnik and Landau [48, 49], supported Korzhinskiĭ's ideas. Later in 1956, Korzhinskiĭ published the derivation of thermodynamic potentials for systems with mobile components in the more internationally respected Russian journal [50]. It seems clear that over the past 50 years, no stimulating information on Korzhinsky's systems has been made to motivate mobile components infiltrating the geologist world into the chemistry realms. Bulach [51], Tretyakov [26, 52], and the Czech textbooks [17, 53] are weighed on Russian books, where the previous [51] contained a special chapter on “Phase diagrams for open systems.” In the 1970s, the study of the equilibrium of oxides with the atmosphere also stimulated industry's interest in the production of new ceramic materials (e.g. ferrites [1, 26]) requiring properties consistent with the process of preparing new high-temperature superconductors. Accordingly, the new thermodynamic school was developed in cooperation between the Czech Academy of Sciences and the Institute of Chemical Technology in Prague, which at that time was prevented by

political repression [54] but revealed in the 1990s [14–16]. Studies of oxide high-temperature superconductors [3–7] then sustained followed by other attractive ceramics, most recently the cobaltite sphere [9–11], which is characterized by its thermoelectric properties. Despite so much work that has been focused on these innovative systems that are interested in variable solid-solid gas interaction [1–11], preferably superconductor stoichiometry [5, 55–61], there is neither sufficient experimental technique nor suitable thermodynamic distinction toward to the theory of partially open systems have become accessible [15, 16], so some real cases are worth example. First, we will show some unique experimental thermoanalytical studies as a special future-oriented experimental solution.

2. Special thermoanalytical measurements applied to nonstoichiometric solids: superconductor example

Alongside ordinary low-temperature magnetic measurements [60] used to determine basic behavior of superconductivity, another specific thermoanalytical technique becomes available elucidating special features of structural behavior. One of such yet unusual diagnostic probe technique is called emanation thermal analysis (ETA) and is based on the specific measurement of radon release. Such a treatment becomes purposely beneficial in the determining fine oxygen changes [61], cf. Figure 2.

Beside the traditional methods based on the mass-changes detection, that is, thermogravimetry—TG or evolved gas analysis—EGA, (see left, thick curves) and their capacity to provide rather insensitive global traces, the method of emanation thermal analysis (upper) brings into play another evaluative possibility. The sample, which is regularly labeled by radioactive thorium, is acting as a recurring source for argon that diffuses and escapes finding the easiest path, so that serving as a well-detected penetrating probe. Argon go-out pathway, forced to march

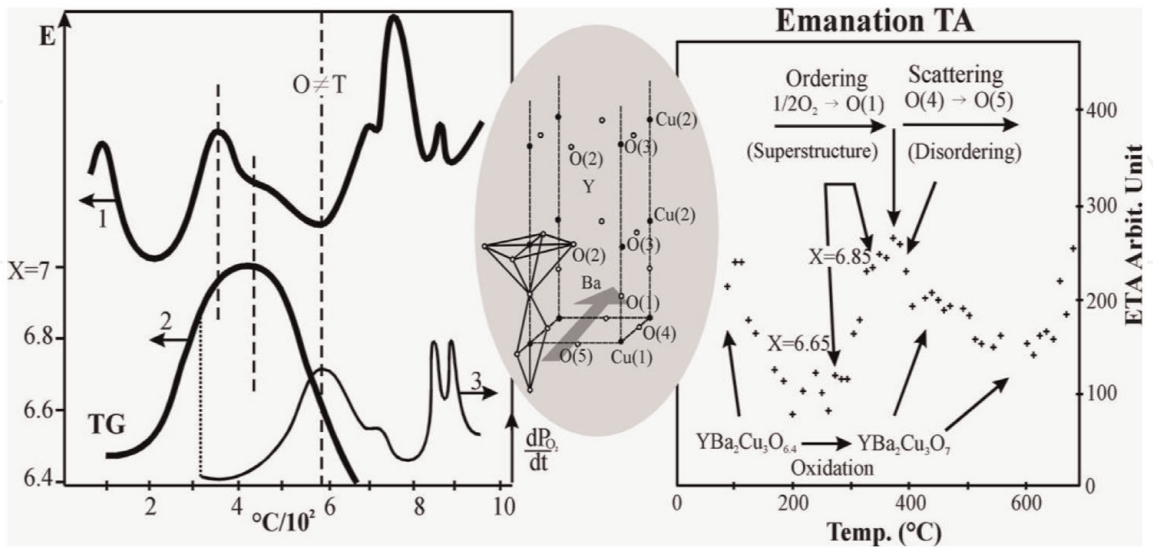


Figure 2. Not so common portrayal for a complex analysis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ behavior when exposed to oxidation changes of variable X . Beside the traditional methods of mass-changes detection (TG-2 or EGA-3, see left, thick curves bottom), the method of ETA, (upper 1) brings into play another more sensitive evaluative possibility. Equipment produced by NETZSCH ltd., (Selb, Germany) has been employed in cooperation with the Czech nuclear research Institute in Řež. The sample is labeled by radioactive thorium, which is acting as a recurring source for argon that escapes functioning as a penetrating probe (upper left and whole right). Particular ordering sequences are illustrated by arrows right.

through the sample bulk, must be receptive and big enough to accommodate such a spacious atom of argon, which is twice as big as oxygen. The best passage is certainly provided by range of defects (i.e. cracks, interfaces), but open network corridors can suit likewise. In this instance where the vacant chains are formed by O(5) voids, we can see it at the inset structure in the middle of **Figure 2**. The continual uptake of the oxygen occupation, which is enlarged along the O(4) voids, can be seen as the step-wise because the more ordered transitional structures (i.e. better superstructures) are gradually created. It reveals that the basic structure of the so-called 123-YBaCu-superconductor stays more complicated, which is closely related to the environmental conditions (temperature, pressure, or transport delays). It follows that intermediate configurations can exist between the familiar fully oxygenated (ortho-) and deoxygenated (tetra-) 123-structures, that is, the superlattice associates with $\delta = 6.55$ [2/500] and $x = 6.85$ [1/300] having complete occupation every two in five and every second chain. Afterward, owing to temperature scattering, oxygen also is inclined to occupy some forbidden O(5) sites, effectively reducing thus the diffusivity free path for the probing atoms of argon through the lattice, see left diagram. Such specificity is provided by the so-called optometric measurements designed to analyze the surface/bulk heterogeneity, which helps revealing its true fractal-like dimensions [62]. For example, the distribution of pore size for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ was calculated from nitrogen adsorption obtaining over the size range between 1.7 and 300 nm and revealing the related fractal dimension, the value of which was calculated to lie close to 2.5.

Yet another type of experimental proof of oxygen arrangement is microscopic observation of the interfacial boundary between 123ortho- and 123tetra-transformations seen in polarized light. Diffusing oxygen builds up the orthorhombic domains with ordered Cu-O chains growing in the direction [110], where the domain density is limited by elastic energy. Upon reaching the critical thickness, the chains begin to grow in a perpendicular direction, thereby forming a double structure as shown in **Figure 3**.

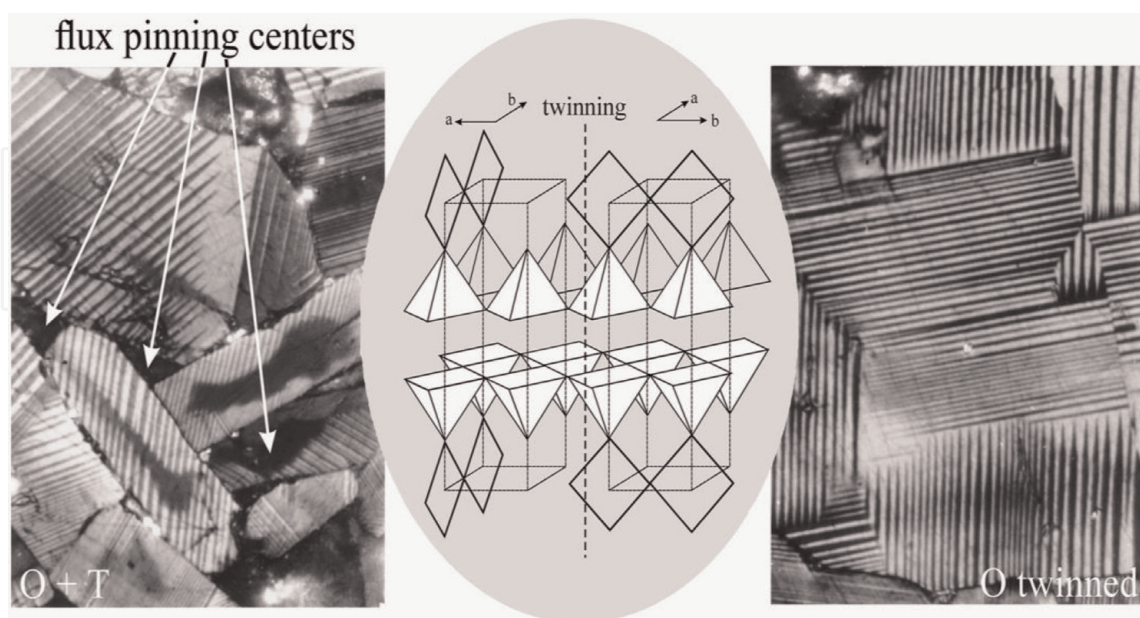


Figure 3. Direct optical observations in polarized light are an excellent aid, showing evidence of orthorhombic domains with the ordered Cu (I)-O chains (striated). The direction of its perpendicular direction is vertically changed as shown by embedded structure, which is under the imperative impact of the energy surface providing a characteristic twinned morphology. In relation to the previous **Figure 2**, it discloses a direct evidence of the elementary processes occurring during the oxygen uptake of $\text{YBa}_2\text{Cu}_3\text{O}_x$ and $\text{O} \rightarrow \text{T}$ transformation, which is another rather sensitive area for further research.

Although we are often able to take care of the so-called off-stoichiometry and the incidence of a second phases in high-temperature bulk superconductors (HTSC), we also have to be aware of the peculiarities of composition at interfaces, where the high curvature $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystals by depletion of oxygen (x) at the surface tension points with subsequent formation of weak bonds. Meanwhile, this can lead to a tail shift of the curve at low temperature, experimentally measured on a graph of relative conductivity versus temperature. Similar effects were previously studied due to the electric field that led to a field-controlled oxygen rearrangement [63] resulting from the movement of mobile charge carriers in the HTSC, which is therefore a generic property of these superconductors.

When conducting SQUID measurements on $\text{YBa}_2\text{Cu}_3\text{O}_x$ single crystals [60], an additional source of curiosity can be created where we can see sequential progression of a step-wise sequential dimensional transfer from the 2-D to the 3-D superconducting state. Although the first indication of superconductivity appears at a temperature of up to 92 K, internal dissipation processes hold its immediate course up to 85 K. This is because the $[\text{CuO}_2]_2$ - layers are more easily rotated to superconducting state after cooling (already at $T_1 = 91.2$ K), while by 2 K lower, it is the same with whole blocks of $\{[\text{CuO}_2]_2- [\text{Y}]_3+ [\text{CuO}]_2\}$ until a total superconductivity is achieved at even 4 K lower temperature through the Ba-CuO-Ba barrier tunnel. However, this behavior is not consistent with classical BCS theory [64], but appears to correlate more with the antiferromagnetic order in a two-dimensional system.

Whereas in the study of conventional superconductors, the main path was made possible by physical measurements, that is, discovery of superconductivity alone, Meissner effect [60, 64], isotope effect, energy gap seen first in specific heat and later in tunneling, etc. In HTSC, the most important test of new theories was performed using a large number of materials in which the CuO_2 planes are built into a completely different ionic background. Chainless materials soon eliminated the very first theories based solely on the superconductivity of CuO chains. Similarly, materials lacking the putative component eliminated apical oxygen ionization, orthorhombic distortion, phonon breeze mode, and other binding mechanisms. The critical test for theories based on the dominant role of the CuO_2 planes was the sensitivity of the critical temperature to the substitution of electronically adjacent zinc to Cu (2) positions.

Another problematic consequence can be found in the HTSC neighborhood of super-current channels, where the cationic stoichiometry may not remain stable, but its intimate bonds can be strongly modified [56, 63]. In this attitude, it can be conceptually assumed that the actual $\text{YBa}_2\text{Cu}_3\text{O}_x$ composition at $x = 6.85$ may contain both divalent and trivalent copper cations as well as holes (\square), such as $\text{YBa}_2\text{Cu}_{2.6}\text{Cu}_{0.4}\square_{0.15}\text{O}_{6.85}$. Due to the negative current charge on very thin adjacent layers, it can cause not only the phase-structure deformation but also some chemical changes due to possible relocation and absorption of some species, most likely Ba^{2+} and \square^{2+} , which can migrate from the inner body of HTSC. The intact interface composition can then alter in an oddly wide range of stoichiometry, for example, $\text{YBa}_{3.03-3.09}\text{Cu}_{0.392-0.26}\text{Cu}_{0.4}\square_{0.223-0.226}\text{O}_{5.744-5.677}$.

3. Definition of partly open systems and the application of hyperfree energy

Lifelong experience with nonstoichiometric materials has always been in search of new expressions particularly seeking new terminology for *partly open* systems consisting of both the *free components* (proficient of exchange between the solid system and its surroundings) and *conservative components* (whose capacity is

remaining constant). Conditions obligatory of the systems' isolation from its surroundings with regard to the exchanging components can be classified in analogy to the standard thermodynamic pairs: *Adiabatic–Isothermal* as well as *Isochoric–Isobaric*.

Therefore, the new-founded pair would construe as [65]: *Isoplectic–Isodynamic* (when *plethos* - *πλήθος* denotes the Greek amount) and *dynamis* (*δύναμις*) meaning a power, strength or ability.

Making use of the above-mentioned terms, the classification of *N*-component systems can be inaugurated. Two different types of components can be comprehended, that is, *c*—conservative (permanent) and *f*—free (mobile), which are satisfying thermodynamic rules $c + f = N$. The *N*-component system with *f*-free components and $c = (N - f)$ conservative components can be identified as a quasi-(*c*)-component system, for example, the system of three components consisting of one free component, which can be called as “quasibinary system.”

On continuing, we can say that it was Holba [54–56, 65–72], who implemented for partly open systems an innovative thermodynamic potential 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.

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

The above symbols are the molar content N_f of free component *f* in the system, where μ_f is its chemical potential. Because the free component *f* is understood to be shared with the surrounding atmosphere (factually serving as a reservoir), its chemical potential in the condensed system is equal to the chemical potential of surroundings. Thus, it is given as a sum of the standard chemical potential and the logarithmic term is involving activity ($\mu_f = G_f^\circ + RT \ln a_f$). Worth noting again is the primary Korzhinskiy's idea [44, 50] as to early distinguish between the mobile (free) components (shared with the surroundings) and the inert (conservative) components, whose pioneering thermodynamic potential μ was brought into play in the area of physical geochemistry. Unfortunately, it did not make a way into to the textbooks of solid-state chemical thermodynamics. This approach is valuable for all transformations involving interaction with the surrounding commonly studied by methods of thermal analysis [18, 73].

For a thermodynamic analysis dealing with partly open systems, it is appropriate to express the composition in terms of *quasimolar fractions* Y_i defined as $Y_i = N_i / \Sigma_c N_c = X_i / (1 - \Sigma_f X_f)$. The related hyperfree energy became thus valuable for the construction of crystal-chemical models allowing the estimation of the relations between the amount of crystal point effects and the equilibrium content of free component [65, 72] in addition to the equilibrium behavior of nonstoichiometric phases [37, 65–76]. In fact, we can observe not only closed systems where each component is isolated from the environment, but also those systems where one component (e.g. water) is exchanged with (i.e. can leak) into the environment, but other components (such as sugar or salt) remain unchanged, which become useful in our test system during processes of drying or baking.

This 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) at the boundaries between the individual phase fields, providing an adaptable mechanism for constructing corresponding potential phase diagrams. Generally, a distinction can be made between sharp and partial phase transitions when crossing phase-field boundaries in this type of phase diagrams, which may be associated with first- and second-order phase transitions in the original Ehrenfest classification scheme,

respectively. However, it should be noted that the latter should not be confused with the critical (or better lambda) phase transition described by Landau. Sharp transitions taking place in the space of variables involving the activity of free components are accompanied by abrupt changes in their content, ΔY_f . Therefore, even if the change in hyperfree energy $\Delta Z_{\varphi-\psi}$ at the boundary between phase fields φ and ψ is zero, its derivatives with respect to free-component activities $(\partial \Delta Z_{\varphi-\psi} / \partial \ln a_f)_{T,p} = \Delta Y_f$, are nonzero and we can use the same approach used to derive the standard Clapeyron equation, for example

$$\left(\frac{d \ln a_f}{d (1/T)} \right)_P = - \frac{(\partial (\Delta Z/T) / \partial (1/T))_{a_f,P}}{\left(\frac{\partial (\Delta Z/T)}{\partial \ln a_f} \right)_{T,P}} = \frac{\Delta H}{R \Delta Y_f} \quad (1)$$

$$\left(\frac{d \ln a_f}{d \ln a_g} \right)_{p,T} = - \frac{(\partial (\Delta Z/T) / \partial \ln a_g)_{P,T,a_f}}{(\partial (\Delta Z/T) / \partial \ln a_f)_{P,T,a_g}} = - \frac{\Delta Y_g}{\Delta Y_f} \quad (2)$$

A more intricate situation occurs when dealing with partial transitions characterized by the beginning of the precipitation of a new phase, where $\Delta Y_f = 0$, since Y_f is a continuous but not smooth predictor function at the boundary delimiting a partial transition, the derivatives of which are subject to sudden changes. In this line of attack, Holba called for the creation of new specialized variables [65, 72] defining a change in the composition of the free component relative to the prediction variables T, p, a_f , and a_g . Analogous to the nomenclature used for similar amounts such as isothermal compressibility or heat capacity, he proposed a new term called *plutability* (derived from the Greek πλούτος = rich, that is, susceptibility to enrichment by a given component). Based on this characterization, we can obtain variables as follows:

$$\kappa_{ff} = (\partial Y_f / \partial \ln a_f)_{T,p}, \kappa_{fT} = (\partial Y_f / \partial \ln T)_{a_f,p} \text{ and } \kappa_{fp} = (\partial Y_f / \partial \ln p)_{a_f,T} \quad (3)$$

which can be, respectively, designated as characteristic expressions, that is *plutability*, *thermal plutability*, and *pressure plutability*.

Respecting the classical approach by Ehrenfest, we can employ the l'Hospital rule on the indefinite forms resulting from (1) and (2) and derive Ehrenfest-like equations involving the changes of plutabilities and other quantities that represent the second derivatives of the thermodynamic potential ($\Delta C_p, \Delta \alpha, \Delta \beta$ standing for heat capacity, thermal expansion, and compressibility changes)

$$\left(\frac{d \ln a_f}{d (1/T)} \right)_P = \frac{\Delta C_p}{R \Delta \kappa_{fT}} = - \frac{TV \Delta \alpha}{R \Delta \kappa_{fp}} = \frac{T^2 \Delta \kappa_{fT}}{\Delta \kappa_{ff}} \quad (4)$$

$$\left(\frac{d \ln a_f}{d \ln a_g} \right)_{p,T} = - \frac{\Delta \kappa_{gT}}{\Delta \kappa_{fT}} = - \frac{\Delta \kappa_{gp}}{\Delta \kappa_{fp}} = - \frac{\Delta \kappa_{gf}}{\Delta \kappa_{ff}} = - \frac{\Delta \kappa_{gg}}{\Delta \kappa_{fg}} \quad (5)$$

4. Practical applicability in Ca-Co-O system

Let us demonstrate the relevance of the above-derived equations on the example of Ca-Co-O system [10, 74] presented in **Figure 4**. The phase equilibria in such three-component system with a single free component (O) can be represented in a so-called quasibinary (i.e. isoactivity section) phase diagram revealed in **Figure 1b**. It exhibits exactly the same topological characteristics as conventional binary phase

diagrams of closed systems. On the other hand, if we affix the cation composition and release the free-component activity, we get an isoplethal, that is, $T - \log a_f$ division presented in **Figure 4a**, for which Eqs. (1)–(4) can be employed. The upper shown two transitions, that is, $(\text{Ca}_3\text{Co}_2\text{O}_6 + \text{Ca}_3\text{Co}_{3.9} + x\text{O}_{9.3-\square}) \rightarrow (\text{Ca}_3\text{Co}_2\text{O}_6 + \text{Ca}_{1-x}\text{Co}_x\text{O})$ and $(\text{Ca}_3\text{Co}_2\text{O}_6 + \text{Ca}_{1-x}\text{Co}_x\text{O}) \rightarrow \text{Ca}_{1-x}\text{Co}_x\text{O}$ (#1 + #2), stay as the distinctive sharp transitions, where the Clapyeronian Eq. (1) is relevant. 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.

By contrast, the lower lying borderline represents a partial phase transition between the solution phase $\text{Ca}_3\text{Co}_{3.9} + x\text{O}_{9.3-\square}$ (misfit phase) and the two-phase region of this phase and $\text{Ca}_3\text{Co}_2\text{O}_6$, whose content is vanishing when crossing the boundary. Hence, the first Ehrenfestian equation must be exploited. 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 begin to decrease at the borderline. Hence, differentiating $\Delta Y_O = (\xi - 1) Y_O + (1 - \xi) (6/5) = 0$ with respect to T and to $\ln p_O$, we obtain

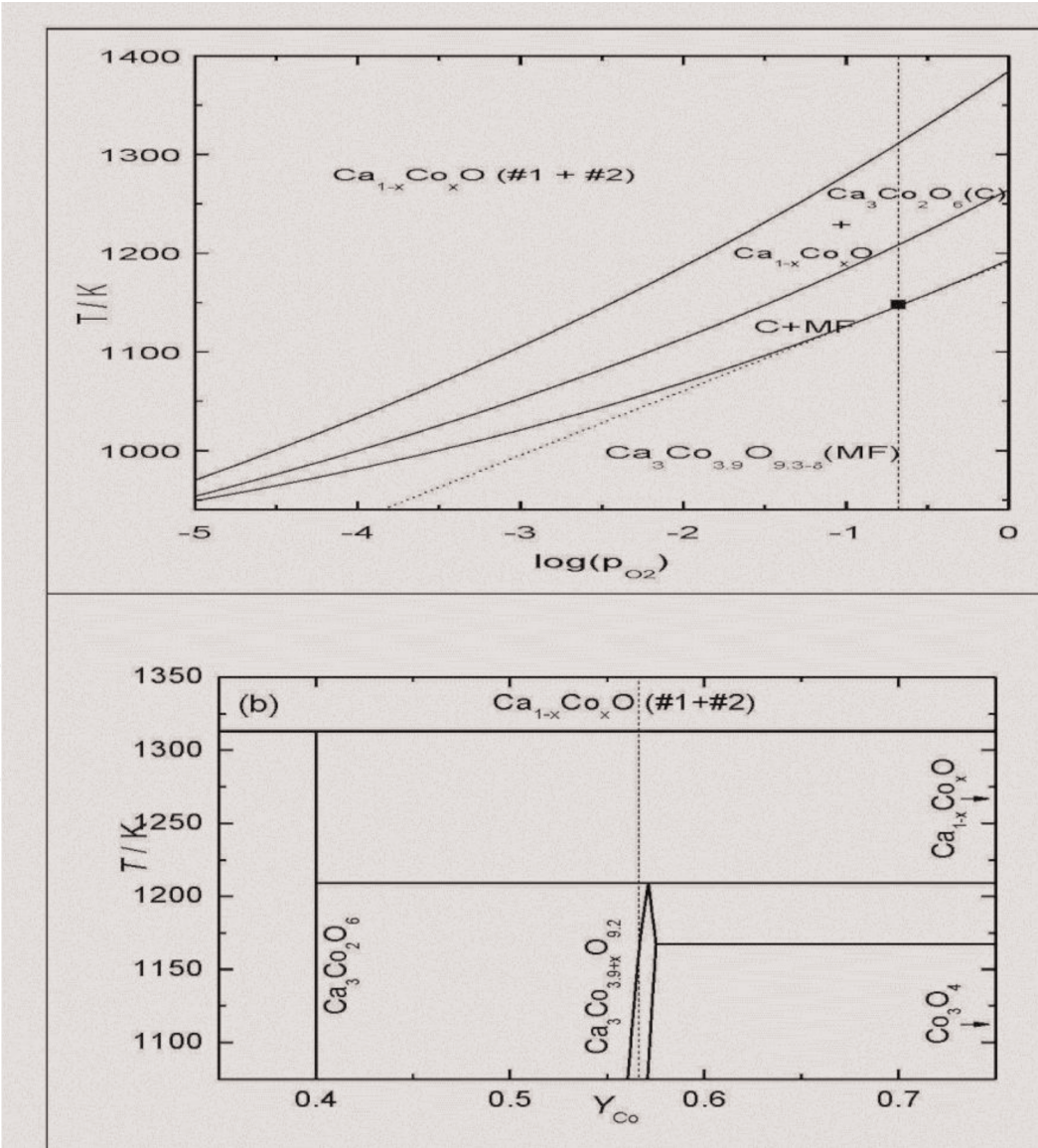


Figure 4. (a—upper) T vs. $\log p_{O_2}$ phase diagram of Ca-Co-O system for Ca:Co = 3:3.9 (b—bottom) T versus Y_{Co} isoactivity section ($p_{O_2} = 0.21$) of Ca-Co-O phase diagram (dashed line—isoplethal section shown in (a)), transferred from Ref. [74].

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

$$\Delta\kappa_{OT} = (\xi - 1)\kappa_{OO} + \left(Y_O - \frac{6}{5}\right) \left(\frac{\partial\xi}{\partial \ln p_O}\right)_{p,T} = \left(Y_O - \frac{6}{5}\right) \left(\frac{\partial\xi}{\partial \ln p_O}\right)_{p,T} \quad (7)$$

and thus

$$\frac{\Delta\kappa_{OT}}{\Delta\kappa_{OO}} = \frac{(\partial\xi/\partial T)_{p,p_O}}{(\partial\xi/\partial \ln p_O)_{p,T}} \quad (8)$$

Borderline should be linear in T provided the $\Delta\kappa_{OT}/\Delta\kappa_{OO}$ ratio was constant, which, however, is obviously not the case as seen from **Figure 4a**; the dotted line corresponds to the integrated Eq. (4) 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. Finally, the both $\Delta\kappa_{OT}$ and $\Delta\kappa_{OO}$ are accessible from experiment. Though, if $\Delta\kappa_{OT}$ can be directly evaluated from TGA data recorded at constant p_{O_2} , $\Delta\kappa_{OO}$ requires a more sophisticated device as is TGA with controlled adjustable p_{O_2} or a coulometric titration. If $\Delta\kappa_{OO}$ is not available, one can take use of another relation resulting from Eq. (4), explicitly

$$\frac{\Delta\kappa_{OT}}{\Delta\kappa_{OO}} = \frac{\Delta C_p}{RT^2 \Delta\kappa_{OT}} = \frac{H(MF) - H(C3C2)}{RT^2(Y_O - \frac{6}{5})} - \frac{H_O^\circ}{RT^2} \quad (9)$$

having a need of the knowledge of enthalpies of both involved phases as well as gaseous oxygen at the transition temperature. This example is supposed to 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.

In conclusion, we can observe from the four new Clapeyronian equations (Eqs. (1) and (2) and two additional involving pressure), the providence of Holba who was able to deduce as many as 28 such pioneering Ehrenfest-like equations published in his last communications [67, 69] and finished just few days before his passing away. It is great pity that such a gifted thermodynamist could not continue publishing his concepts thus far capable of additional publications in the form of future paper.

Concisely, let us highlight that the concept of hyperfree energy and a new class of Clapeyron and Ehrenfest-like equations can be found useful for the equilibrium studies and construction of thermodynamic models of nonstoichiometric phases [65–76]. It became useful for structuring of straightforward phase diagrams reflecting the equilibrium phase relations under a given controlled atmosphere [65, 73]. The impact of Holba toward better understanding of a thermodynamic background of processes [13, 18, 65] and his encouragement of novel thermodynamic portrayal of partly open system [15, 16, 54] is unlocked to a wider attention laying emphasis on the fact that he was one of the cofounders of the renowned Czech thermodynamic school [17, 20, 72, 77, 78], cf. **Figure 1**. It is investigated in the early issues of the local Czech journal *Silikaty-Ceramics* published in Prague [13, 14, 18]. Holba's noteworthy legacy throw out becoming prominent within Russian circles [73, 76] and it gave stimulus for Holba's awarding the prestigious Russian Kurnakov medal of the Russian Academy of Science in the sphere of thermodynamics conferred in memoriam during the XV International Conference

on Thermal Analysis held in Saint Petersburg 2016. So, this chapter is also devoted to his commemoration.

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