

ON CHRONICLE AND RECENT EXPLOIT OF A SPECIAL CLONE OF FREE ENERGY (HYPER) BENEFICIAL TO THERMODYNAMIC DESCRIPTION OF PARTIALLY OPEN GEOLOGICAL, METALLURGICAL AND OTHER NONSTOICHIOMETRIC SYSTEMS

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Abstract

Founding and determination of thermodynamic functions related to solid often geologic materials is traced showing interactions between Czech Professor F. Wald and Russian R.S. Kurnakov and D.S. Korzhinskiĭ in the early definition of phases and characterization of partly open systems. Development of thermodynamic notions regarding solid-state-gas description by P. Holba is reviewed showing its consequence in geology and metallurgy. For the joint definition of operate of mobile components the hyper-free energy was developed and recently put into function in nonstoichiometric systems. Novel even if unusual term of the associated new variable plutability is explained. Instigators of modern thermodynamic educate in both the Czechia and Serbia is made more noticeable.

Keywords: Thermodynamics; Wald; Korzhinskiĭ; Holba; Nonstoichiometry; Mobile components; Hyper-free energy; Plutability.

Dedication: Dedicated to Prof. Dragana Živković Dr.Sc. (1965-2016) one of the distinctive metallurgists, the member of Serbian Academy of Engineering, who promoted thermodynamic education in Serbia and helped cooperation with the Czech Pilsen Westbohemian University and Prague Institute of Physics.

1. Historical introduction

The quantity called free energy is well known as a more advanced form for the outdated term affinity, which was used by chemists in the earlier years of physical chemistry to describe the force that caused chemical reactions. Toward the end of nineteenth century Josiah Willard Gibbs (1839-1903) published method of geometrical representation of the thermodynamic properties of substances in which he sketched the principles how estimate the tendencies of various natural processes to ensue when bodies or systems are brought into contact. It became necessary to distinguish part portion, component or constituent which by using the Gibbs' phase rule published in his landmark paper "On the Equilibrium of Heterogeneous Substances" is appropriate to non-reactive multi-component heterogeneous systems in thermodynamic equilibrium. The inherent dimensionality D is given by the equality $D = C - P + 2$

where F is the number of degrees of freedom, C is the number of components and P is the number of phases in thermodynamic equilibrium with each other. The number of degrees of freedom is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature T , pressure P or chemical potential μ that can be varied simultaneously and arbitrarily without affecting one another. In partly open systems, however, dimensionality can be conveniently visualized involving the standard intensive quantities (T, P, μ) as predictors while the stoichiometry of conservative components is assumed either uniquely given (single conservative component) or otherwise kept fixed so $D = C - P + 2 - I$ where I means the number of fixed predictors lowering the total dimension $C + 1$ of the phase diagram.

The novel term stoichiometry was introduced into chemistry at the turn of eighties by Jeremias Benjamin Richter (1762-1807) to point out an experimental

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finding that substances combine together in fixed weight ratios. Richter's results was then attached to German translation of Berthollet's treatise „Recherches sur les lois de l'affinite“ and became an impulse to formulate the law of definite proportions which provided an important support for Dalton's atomic hypothesis. Berthollet, however, did not accept the general validity of this law and contended that fixed ratios are rather an exception. After one century the first nonstoichiometric compound – palladium hydride – was discovered, however, intermetallic phases were not yet considered as compounds at that time. The almost unknown considerations on the relations between the terms phase, compound and solution became a concern of Czech analyst in metallurgy František Wald (1861-1930) which is worth of making more obvious.

One of the most important thermodynamic basis looked for the relation between component, chemical potential and phases which can be traced back to some Czech-Russian contemplation the first reflection of which was offered by F. Wald, later Rector of the renowned Czech Technical University in Prague) in his early publications [1]. In particular these Wald's considerations led in 1912 Russian Nikolai Semenovich Kurnakov (1860-1941) [2] to publish definition in which compounds (those obedient recognizing the so far standard situations) were named as *daltonides* while nonstoichiometric compounds were called *berthollides* [3, 4] in honor of the scientist who called into question the general validity of definite proportions law more than one century before. This idea was continued via detailed examination of nonstoichiometric oxides by Yurij Dimitrivich Tretyakov (1931-2012) [5]. It is interesting that Kurnakov's student (and co-author of the article, in which berthollide name was first used [3]) was Aleksander Iljič 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 Hendrik Willem Bakhuis Roozeboom (1854-1907) who applied Gibbs phase rule to alloys (1900) [6, 7] writing a fundamental book on phase equilibria. The remarkable Lewis' important concept of „activity“ (1907) [8] brought a more practical form of chemical strength of component and practical depiction of „negative decadal logarithm of H^+ activity“ suggested by Sørensen two years later (1909) [9] today's known as pH quantity. In 1923 the subsequent development of thermodynamics was accomplished by Lewis new book [10]. Another attempt to overcome the traditional limits of closed systems was in 1944

accomplished by Ellingham [11]) showing the relationships between decomposition temperatures of various metal oxides in terms of ΔG vs T plot. In 1948, Richardson & Jeffes [12] 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 [13] on equilibrium nonstoichiometry 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 [14], which presented phase diagrams obtained under conditions of partly open systems, e.g., under air atmosphere or in the contact with liquid iron. A different application, which was overcoming the standard concept of closed systems, was established through the 1946 study by Pourbaix [15], who suggested the diagrams consisting of the plot of redox potential (E) versus acidobasic potential (p_H) to portray equilibria of dilute aqueous solution at room temperature. Associated applications became widely known in hydrochemistry probably due to books by Garrels [16] and Garrels & Christ [17].

In 1936 Dmitrii Sergeevich Korzhinskiĭ (1899-1985) distinguished two classes of components in geochemical systems [18, 19]: inert components whose amounts (masses or numbers of moles) are independent on amounts of any other component and on 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 studies of real material systems in chemistry, geochemistry, metallurgy, hydrochemistry and material science. Korzhinskiĭ also helped to develop the physicochemical basis for analysis of mineral parageneses revealing it for 1957 publication [18]. According to that book, translated into English in 1959 [19], Korzhinskiĭ analyzed the relationships between the mineralogical composition and the values of chemical potentials of components as early as in early 1930's [20] providing the concept of thermodynamic potentials for systems with wholly mobile components. Worth noting is Korzhinskiĭ's distinguishing two classes of components in geochemical systems as early as in 1936 [20], i.e. 'inert components' whose amounts (masses or numbers of moles) are independent on amounts of any other component and on processes inside the system, and 'perfectly mobile components', whose chemical potentials (or other intensive parameters) are



independent factors of equilibrium. Nevertheless the applications of Korzhinskiĭ's new potentials [21, 22] were first rejected by geologist Nikolajev [23] but publications of Verhoogen [24] and Thompson [25] and also paper by Palatnik & Landau [26] supported Korzhinskiĭ in thoughts. Later in 1956 Korzhinskiĭ published derivation of thermodynamic potentials for systems with mobile components in a more internationally available Russian journal [27].

2. Associated focal points of development

It seems be evident that during the last half of century no information on Korzhinskiĭ's systems counting mobile components were capable infiltrating from the world of geologists into the world of chemists counting the Russian book by Bulach [28] and the more recent Czech textbook [29] which included a particular chapter „Phase diagrams for open systems“. In 1960s the study of equilibria of oxides with atmosphere was also stimulated by the industry's interest in order to produce new ceramic materials (e.g. ferrites) of required properties using an adequate high-temperature preparation procedure. In the 1970's, at the Czech Institute of Physics, a detailed research focused on ferrites [30] and latter stretched out to superconductor oxides [31, 32]. This subject was generally extended to various oxide mixtures [33] carried out in most countries but in spite of so much work concentrated on these systems with a variable solid-gas interaction no adequate application towards the partly open system was conquered to their thermodynamic studies.

Pavel Holba (1940-2016) as a member of group of young scientists, were studying the properties of ferrites [30] as a branch of solid-state chemistry and associated thermodynamics [34]. They profited from then popular textbooks on thermodynamics by Šatava [35] and Swallin [36] but capable of reading Cyrillic alphabet (Russian or Serbian texts) they got inspired at that time internationally unknown Russian papers (e.g. Tretjakov [5] or Korzhinskiĭ [18]) proficient of understanding then atypical texts. They were carrying out some thermogravimetric investigations looking for a better adapting Gibbs free energy as a more adequate tool for describing the equilibria of solid oxides with gaseous surroundings. It involved incorporation of the so called equilibrium background of processes studied under heating [37] trying to develop better theoretical basis of thermal analysis. Even if P. Holba was permitted to leave to Moscow to stay whilst collaborating with Prof. Ju. D. Tretjakov [5, 37], his conclusions were at that time constrained by political discrimination of liberal publishing becoming fully available with a delay in the 1990's [38]. Holba then continued in researching of above mentioned nonstoichiometric oxides, particularly

paying attention to copper-based superconductors [31-33] which culminated in wider theoretical studies during 2010's [38-41].

Long lasting experience with nonstoichiometric materials have needed of coining a new terminology such as 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). Conditions necessary of the systems' 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: isoplethic – isodynamic when plethos (*πλήθος*) denotes Greek amount and dynamis (*δύναμις*) meaning 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 ($C + f = N$), can be comprehended. The N-component system with f-free components and C equal to (N - f) conservative components can be identified as an N-component system with c-conservative components, e.g., the system of three components consisting one free component can be called „quasibinary system“ [41, 42].

3. Approach to hyper-free energy

Although the scheme of interaction of conservative against mobile components seems a bit complicated it bears quite simple rudiments. So on continuing the story of partly open systems we can articulate that it was indisputably P. Holba [24-28] who implemented an innovative thermodynamic potential applicable to nonstoichiometry thermodynamics. He thus mold rediscovering and properly implementing the correct meaning of the earlier known hyper-free energy Φ . It is defined as a Legendre transformation of the standard Gibbs free energy, G, through $\Phi = G - N_f \mu_f$ via the specification $\Phi = f(T, P, \{N_c\}, \{\mu_f\})$ 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 activities. Worth noting again is the primary Korzhinskiĭ's idea [10, 15] to early distinguish between the mobile (free) components (shared with the surroundings) and the inert (conservative) components attached with solid whose pioneering thermodynamic potentials *F* was



used in physical geochemistry, but unfortunately did not penetrate to the textbooks of solid-state chemical thermodynamics [27]. This approach is valuable for all transformations involving interaction with the surrounding commonly studied by methods of thermal analysis [40].

Let us remember that for the thermodynamic analysis of partly open systems it is appropriate to express the composition of N components (of which $N-2$ are conservative components) and two further free components – with the indices f and g . Associated *quasimolar fractions* Y_i can be customarily derived from molar fraction $X_i = Y_i / (1 + Y_f + Y_g)$. Associated mode of hyper-free energy become useful for the construction of crystal-chemical models allowing estimating the relations between, e.g., the amount of crystal point defects and the equilibrium content of free component [38, 39] in addition to the description of equilibrium behavior of nonstoichiometric phases [41]. In reality we can observe not only the closed systems whose every component is isolated from the surroundings but also such pioneering systems whose one component (e.g., water) is exchanged with (i.e., can escape into) the surroundings but other components (as e.g. sugar or salt) remains in our system unchanged (during e.g. drying or baking), of course, apart from the most interesting geological or metallurgical systems which are able to release or absorb oxygen.

Such a concept became useful for an extended deriving the related Clapeyron-like equations applicable for partly open systems in which the approach by Holba challenged to coin new specialized quantities [39-41]. However, it is nothing anxious when further defining the standard variation of free component composition (\sim activity a) with respect to the so called predictor variables T, p, a_f, a_g .

Nevertheless it would generate a requirement to coin yet new, even if somehow strange, idiomatic variables such as pioneering parameter *plutability* (newly derived from the Greek $\pi\lambda\omicron\upsilon\tau\omicron\varsigma$ = rich) in the form of $\kappa_{\text{ff}} = (\partial Y_f / \partial \ln a_f)_{T,p}$ as well as further quantities, named as:

$$\text{thermal plutability } \kappa_{\text{ff}} = (\partial Y_f / \partial T)_{T,a_f},$$

$$\text{pressure plutability } \kappa_{\text{fp}} = (\partial Y_f / \partial P)_{T,a_f},$$

$$\text{and even mutual plutability } \kappa_{\text{fg}} = (\partial Y_f / \partial \ln a_g)_{T,p,a_f}$$

which was in details explained in the current book chapter [41]. Since the variation of Y_f is a continuous but not a smooth function of predictors (T, p, a_f, a_g) whilst on the borderline delimiting a partial transition, ΔY_f which is equal zero at the transition point. The plutabilities are, however, discontinuous stepwise functions with $\Delta k_{fi} \neq 0$ at the point of transition.

From the Clapeyron-like equations [41] we can obtain the first (standard) Ehrenfest-like equation by differentiation at a constant pressure with respect to temperature, while the second Ehrenfest-like

equations are further derived by differentiation again with respect to pressure under the application of Maxwell relation $(\partial \Delta_d S_q / \partial p) = -\partial \Delta_d V_q / \partial T$.

These new Clapeyron-like equations correlate the mutual variations (derivatives) between pairs of three intensive potential quantities (T, P, a_f) with the changes of several relative (i.e. quasimolar) quantities $\Delta_d H_q, \Delta Y_f, \Delta_d V_q$. It means that from a single one Clapeyron equation we should be able to derive six Ehrenfest-like equations via three differentiations with respect to T, P , and a_f plus another three to distinguish comparisons and relationship between $T-P, T-a_f$ and $P-a_f$. Somewhat unusual yet higher, i.e., the third type of Ehrenfest-like equations transpire obtaining by auxiliary differentiation with respect to the logarithm of the free component activity, such as:

$$\begin{aligned} \{d \ln a_f / d(1/T)\}_P &= -T^2 (\Delta_i \kappa_{\text{ff}} / \Delta_i \kappa_{\text{ff}}) \\ &= (T^2 \Delta_i \kappa_{\text{ff}}) / (\Delta_i \kappa_{\text{ff}}) \end{aligned}$$

yielding for example correlation between heat capacity C_p and thermal expansion a in the form $\Delta_d C_p / (\Delta_d \kappa_{\text{ff}}) = -(T_i V_q \Delta_d a) / (\Delta_d \kappa_{\text{ff}})$ which gives a rather complicated appearance of a range of equations impossible to encapsulate herewith only providing thus a provisional cast look. Conclusively P. Holba derived as many as thirty-one such pioneering equations published in his last communication [28] completed just few days before his death. It is great pity that such a gifted thermodynamist could not carry on his publishing pursuit stretching his concepts to become a part of regular paper.

4. Conclusion

The hyper-free energy and new class of Clapeyron-like and Ehrenfes-like equations can be found functional for equilibrium studies and building of thermodynamic models of nonstoichiometric phases [39-41] as well as for the construction of simple solid-state phase diagrams reflecting the equilibrium phase relations under a given controlled atmosphere. The subject of free interaction between conservative solid components and mobile components in the surrounding atmosphere became an important subject of books in geology [42, 43], metallurgy [44, 45] and other nonstoichiometric ceramic systems [46-48]. The topic was also a theme of lasting Czech-Serbian cooperation - see photo.

The famous Šatava's Czech thermodynamic school [35] influenced Pave Holba to get to a better understanding of the thermodynamic background of processes [49], crystallization kinetics of glasses [50, 51] putting together his early encouragement toward a novel thermodynamic description of partly open system [41].



This novelty is worthy drawing to a wider public attention as well as the innovation made available thanks to Dragan Živković and when caring for and inspiring theory of phase diagrams [52-55] and overall grade of engineering technology [56]. At the same time emphasis should be laid on the fact that they were one of the welcomed instigators of modern thermodynamic educate in both the Czechia [46, 47] and Serbia [45, 56].



Photo: Dissertation photo of Dragana Živković (from left) at the board of Jaroslav Šesták, Ilija Ilić and Živan Živković. The Czech-Serbian cooperation strengthen during the ICTAC 1985 conference in Bratislava and lasted until now despite the hard time in late nineties affected by the so called „humanitarian“ (NATO) bombing of former Yugoslavia, which the papers' authors experienced personally.

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