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# CHEMICAL POTENTIALS AND ACTIVITIES IN METALLURGICAL PROCESSES

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The analysis of the correct calculation of chemical potentials of components in metallurgical processes is provided and the importance of the proper selection of the reference state is highlighted. This has direct implication on correct calculation of activity which must follow the principles of thermodynamics and be suitable for practical application in pyro- and hydrometallurgical processes. Ref. 9, fig. 1.

*Key words: thermodynamics; Gibbs energy; chemical potential; solutions; activity; melts*

All metallurgical processes involve generation, handling and treatment of different solutions: metallic, sulfide or oxide melts (pyrometallurgy), aqueous liquids and suspensions (ore dressing, hydrometallurgy). These solutions may comprise only few components like Fe–Si–C or Fe–Mn–C, or can have dozens of components in complex alloys and slags. In all the cases knowledge of the correct thermodynamic properties of the components of these solutions as function of temperature and composition is of a paramount importance for design of a metallurgical process and its optimization to maximize useful element extraction at minimal costs, emissions and energy requirements.

The direction and extent (the equilibrium state) of a process can be predicted by the combination of the Gibbs energy of phases and material balance at each temperature and pressure. For a process to be thermodynamically possible, this combination should lead to decrease of the total Gibbs energy of the reacting system. This imposes the tendency of equalization of temperature (thermal energy), pressure (mechanical energy) and chemical potentials of all the species within the system (melts in the furnace with the slag and gas phases). It is known that equilibration of chemical potentials may take place through both matter transformation (chemical reactions within the phase and between the phases) and transport processes (diffusion of species from areas of higher chemical potentials to areas of lower chemical potentials, convection and associated phase transitions). Here we will address the first part — the definition and transformation of chemical potentials in chemical sense, relevant for correct description of the metallurgical processes.

For an accurate depiction of the processes involved solutions, a consistent thermodynamic description of the species chemical potential and the free energy is required. Equilibrium calculations must also take into account the selection of the correct reference state and concentration dependence of chemical potentials (or activity coefficients) in the solution range, which rather often is not treated in a proper way. In this analysis, we revisit the definition and formulation of both activities and chemical potentials and address the limitations imposed on their calculation and application.

**Theoretical background.** At constant temperature ($T$) and pressure ($P$), the driving force for a process is the tendency to the minimization of free energy of the system. Even the equilibrium state is not fully achieved, the path for free energy minimization tells about the extent when the process might be implemented. In most metallurgical processes $T$ and $P$ are fixed or known, and the direction of individual processes can be analyzed by Gibbs energy $G(T) = H(T) - T \cdot S(T)$, where $H(T)$ is the enthalpy and $S(T)$ is entropy. The partial Gibbs energy of the component (i.e. the chemical potential $\mu_i$ of this component) is defined as change of the molar Gibbs energy with increasing number of moles of this component $n_i$, keeping $T$, $P$ and other components amount ($n_j$) constant, whereas the molar fractions of the components $X_j$ cannot be held constant:

$$\mu_i = \bar{G}_i = \left.\frac{\partial G}{\partial n_i}\right|_{n_j,T,P} \neq \left.\frac{\partial G}{\partial X_i}\right|_{X_j,T,P}. \qquad (1)$$

Here is the first source of the common mistake: the derivation of the free energy to obtain chemical potential is sometimes done by its concentration and not by number of moles of the selected component. The definition of the chemical potential (1) clearly states that all molar amounts (and not concentrations) of other

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components must be kept constant during the derivation. The second common mistake is in ignoring the mathematical procedure limitations. Implementation of derivation in (1) for a component *i*, the free energy *G* must be 1) continuous, 2) differentiable function of the amount of the substance *i* in 3) existing homogeneous solution phase. The chemical potential has to be therefore achievable in real (and not hypothetical) solutions that must exist across the whole considered concentration range. If this is not the case, the Gibbs energy function is not continuous and cannot be differentiated in the required domain — then chemical potential cannot be determined within the Gibbs thermodynamic formalism.

Third source of errors might arise when the Maxwell's relations for partial derivatives are not held for data used for calculation of the chemical potential [1]:

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_k} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{n_i}. \quad (2)$$

Here derivation is again performed by number of moles and not by molar/percentile fractions, as in the latter case it is impossible to preserve the total number of moles of other components in the system [2] violating conditions (1). In the case of equilibrium, the change of Gibbs energy ($dG$) must approach zero:

$$dG = 0 \rightarrow VdP + SdT + \sum_i n_i d\mu_i = 0, \quad (3)$$

which is a well-known Gibbs–Duhem equation. From (3) it follows that at $dT = dP = 0$ the equilibrium state requires no further changes in the chemical potentials of the components in all phases, as the amount of species is always positive.

An expansion of the calculation to multi-component solution becomes more complex for each additional component, because all chemical potentials must be recalculated by correct derivation. This makes direct use of chemical potential in metallurgical practice rather challenging. Hence for practical reasons it is more convenient to use activity $a_i$, linking the chemical potential of the component $\mu_i$ to its molar concentration $X_i$ in relation to the reference state $\mu_i^0$:

$$a_i(X_i) = \exp\left(\frac{\mu_i(X_i) - \mu_i^0}{RT}\right);$$
$$\mu_i(X_i) = \mu_i^0 + RT\ln(a_i(X_i)) = \quad (4)$$
$$= \mu_i^0 + RT\ln(\gamma_i(X_i)\cdot X_i).$$

Activity (together with the activity coefficient $\gamma_i$) of a component is a measure of «effectiveness» of the component in that particular solution in respect to its reactions with other components. Classical (Raoult) definition of activity relates it to the partial pressure of the dissolved component in a solution vs. its reference state as pure substance:

$$a_i(X_i) = P_i(X_i) / P_i^0, \quad (5)$$

where $P_i$ is the partial pressure of this specie and $P^0$ is its pressure in the reference state (giving $a_i^0 = 1$). The reference state assigned to the pure substance is taken by default by many thermodynamic calculations. However, for metallurgical system it is confusing to use e.g. pure sulfur relating this to melts of 1873 K temperature.

When concentration of one component is low (as often assumed also in aqueous solutions), often a Henrian reference state is assumed — there activity coefficient $\gamma_i$ there is taken as a constant (in ideal solutions, $\gamma = 1$ in the whole concentration range). This has a limited application to «dilute» solutions only, but in general case that degree of dilution cannot be rigorously assigned with some numerical value (0.2 % Cr in iron might be considered «dilute», but 0.2 % O is likely not). A solution seen as a «dilute» from a practical point of view, might not at all be dilute in Henrian sense [2].

The reference state selection is therefore of a paramount importance in chemical thermodynamics, as wrong or incompatible states make respective thermodynamic calculations useless. Historically in metallurgy it was not uncommon to take the reference state as 1 wt. % of the substance in the solvent (for example, in the steelmaking 1 % oxygen in liquid iron at 1873 K, even such solution does not exist). However, as shown in [2–4] such selections are wrong and should not be used. Despite some handbooks are stating that the selection of the reference state is a matter of taste and usability, any such selection should not violate basic thermodynamic principles.

**Correct definition and calculation of activities**. Following the basic thermodynamic principles, it is possible to formulate rigorous conditions for activities and chemical potentials calculation:

the Gibbs energy function must be a continuous and differentiable by the amount of the substance in the solution phase, and this solution must really exist, not being hypothetical (otherwise the derivation in (1) cannot be performed);

the chemical potential and thus activity of the component must be real, measurable and continuous functions in the solution phase. Every correct reference state must be achievable within the proper concentration range;

the activity function of any component must fulfill the following three relations:

$$\left.\frac{\partial \ln a_i}{\partial T}\right|_{P,X_{i,j,k}} = -\frac{\Delta\bar{H}_i - \Delta\bar{H}_i^0}{RT^2};$$

$$\left.\frac{\partial \ln a_i}{\partial P}\right|_{T,X_{i,j,k}} = \frac{\bar{V}_i - \bar{V}_i^0}{RT}; \qquad (6)$$

$$\left.\frac{\partial \ln a_i}{\partial X_i}\right|_{T,P,X_j/X_{k(j,k\neq i)}} > 0,$$

where superscript 0 indicates respectively partial enthalpy $H_i$ and partial molar volume $V_i$ in the reference state. Note that in (6) the requirement of constant number of moles $n_i$ has been converted to the requirement of constant ratios of concentrations of other components ($X_j/X_k$) as we have transformed chemical potentials $\mu_i(n)$ to activities $a_i(X)$;

the reference state must always be achievable by a continuous changing of the substance concentration keeping the same solution (phase) structure type, and it has always unity value of the activity;

the activity of a component in the absence of that component must be zero.

For the solutions which do not cover the whole composition range (e.g. in the case of saturated limit such O or C in Fe-based systems), the reference state cannot be chosen as pure component (5), since the third rule (6) would be violated and in the first and second equations (6) partial enthalpy and partial molar volume would be unobtainable. Here the reference state must be chosen at the substance saturation point, when all three relations (6) hold. This is shown in Fig. 1, *a* for ideal solution and Fig. 1, *b* for limited solubility of the component *B* in *A*.

A special case for activities calculation which is also prone to common mistakes is for solutions having charged species (ions) such as oxide melts (slags) and aqueous systems. The major difficulty is impossibility of definition of the chemical potential in a standard Gibbs way, because it is not possible to increase number of moles of any ion without simultaneous changing the equal amount of a counter-ion. In other words, it is impossible to just add or subtract electrons to/from the system without breaking the electroneutrality conditions [5]. Only concentration of a pair of ions (cation – anion) of equal charges could be theoretically varied, and hence commonly seen in literature diagrams as function of pH or $SiO_4^{4-}$ concentration are not thermodynamically correct diagrams [7].

The serious thermodynamic failure of this approach is artificial separation of the main component

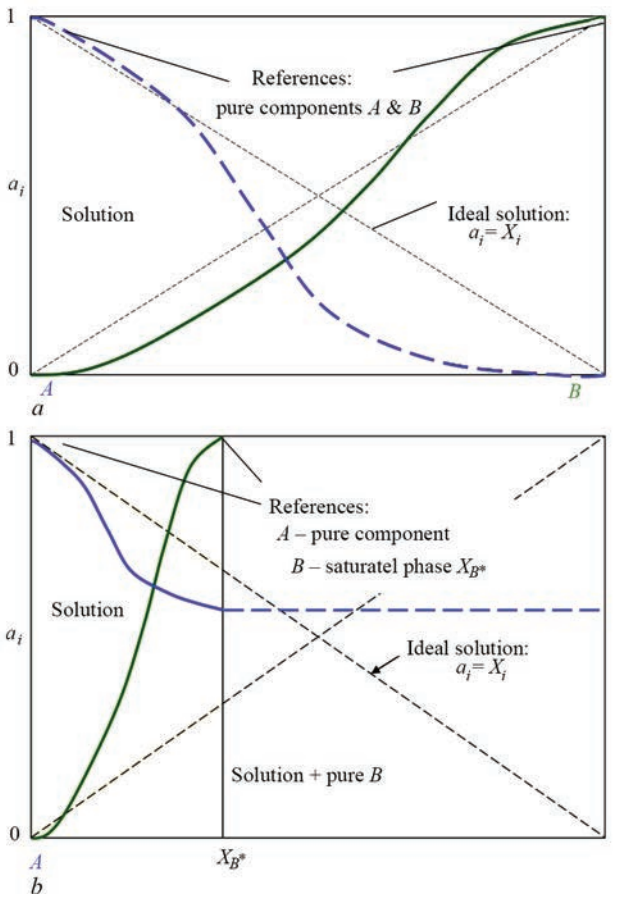


Fig. 1. The schematic illustrating selection of correct reference states for ideal *A–B* solution (*a*) and for a limited solubility of *B* in *A* (*b*). In the second case, the correct reference for *B* is the saturated solution at the concentration $X_B$*, as in the two-phase area there is no changes in composition of the phases, only in their amounts

(solvent) from others (solutes), making the system non-symmetric, and use of molality scale, which automatically excludes the whole composition range, as was pointed out in [3, 4]. Many such hypothetical reference states, previously used in metallurgical practice for years, are therefore lacking rigorous background although they can be applied in engineering calculations. These states do not generally satisfy the main thermodynamic rules and thus cannot be recommended [3, 6].

In earlier developments of thermodynamics of metallurgic processes, Wagner formalism with Taylor's series expansion of the activity coefficient was conventionally used [2, 6] when the reference state was chosen as 1 wt. % of the component (even this solution could not exist). This mislead to results when such activities are being attempted to equilibrate with other phases and such method should not be used [6, 7]. Taylor's series expansion is only valid within the vicinity of the differentiation (expansion) point and might not be extrapolated over the wider concentration range. Hillert [4] has also shown that traditional Wagner's expressions for free energy are invalid in

respect to the Gibbs–Duhem equation, unless a special correction term is added. At such conditions, this may lead to thermodynamically impossible phase diagrams, which cannot exist in reality [7, 8].

**Suggested calculation procedure.** The chemical potential of a component in the multi-component solution can be expressed in terms of molar fractions and the integral molar Gibbs energy $G_m$:

$$\mu_i = \left(\frac{\partial G_m}{\partial n_i}\right)_{n_j} = G_m + (1 - X_i) \times \times \left(\frac{\partial G_m}{\partial X_i}\right)_{X_j/X_k} - \sum_{j \neq i}^{K-1} X_j \left(\frac{\partial G_m}{\partial X_j}\right)_{X_j/X_k}, \quad (7)$$

which allows calculation of for any cross-section of the compositional space by derivation of Gibbs energy. Special care must be taken when selecting proper concentration paths for free energy and chemical potential calculation, because in a multi-component system it may depend on the integration path. Taking into account the last rule of (6), the derivative of chemical potential of a component by its molar fraction (and not by number of moles) takes the form at $X_j/X_k$ = = const:

$$\left.\frac{\partial \mu_i}{\partial X_i}\right|_{X_j/X_k} = (1 - X_i)\left(\frac{\partial^2 G_m}{\partial X_i^2}\right)_{X_j/X_k} - \sum_{j \neq i}^{K-1} X_j \left(\frac{\partial^2 G_m}{\partial X_j \partial X_i}\right)_{X_j/X_k} > 0, \quad (8)$$

where the $G_m$ term includes 1) the sum of the reference free energy terms, 2) mixing entropy of ideal solution and 3) the excess Gibbs energy responsible for the deviation from the ideal behavior:

$$G_m = \sum_k X_k G_k^0 + RT \sum_k X_k \ln X_k G_m^{ex};$$
$$G_m^{ex} = \sum_{n=0,1,2\ldots} \sum_{i \neq j} X_j X_i L_{ij}^{(n)} (X_j - X_n)^n; \quad (9)$$
$$L_{ij}^{(n)} = A_{ij}^{(n)} + B_{ij}^{(n)} T,$$

with interaction parameters $L^{(n)}$ of second and higher orders of $n$ are temperature-dependent (ternary and higher parameters also can be added). Extended Gibbs–Duhem equation (7) is well known, but its direct application in metallurgical practice is not straightforward if the reference data are not well defined (for example, taking pure liquid oxygen at 1873 K as a reference for Fe–Mn–O system is clearly an improper choice). Application of (8) eliminates the reference Gibbs energies as they become a constant term in both terms of the equation. Furthermore, selection of paths of $X_j/X_k$ = const and making the calculations for each of them simplifies the procedure. In a ternary system like Fe–Mn–O fixing $X_{Fe}/X_{Mn}$ = const automatically makes Gibbs energy dependence at constant temperature only from $X_O$ because of the equalities

$$X_{Fe} + X_{Mn} = 1 - X_O;$$
$$\frac{\partial X_{Fe}}{\partial X_O} = -\frac{1}{1 + X_{Fe}/X_{Mn}} = \text{const}. \quad (10)$$

Hence most of cross-derivatives in (8) even those not directly including $X_O$ could be considered constants at $T$, $P$ = const, and the calculation could be straightforward. The validity of rules (6) is fulfilled when the non-negativity condition (8) holds. Calculation of activities will be performed backwards after the chemical potential derivative (8) is properly accessed, and not by the opposite (guessing reference for activity and then calculating chemical potential based on that). This procedure allows an adequate assessment of thermodynamics of metallurgical systems without presuming the reference state for activity [8]. For example, data in [9] clearly show that activity of carbon in Fe, Ni and Co melts exactly reaches unity at saturation concentration of carbon (and not at 100 % C as pure graphite) for each specific temperature thus fulfilling the conditions (6) explicitly.

## Conclusions

1. Carried out thermodynamic analysis has highlighted the importance of correct determination and calculation of chemical potentials and activities of components in metallurgical processes.

2. For any system, a reference state selected for any of the components must obey the thermodynamic rules shown above to be mathematically and physically correct. Previously this had many computational challenges, but they are not anymore problem with modern computing methods.

3. For practical applications the starting point for selection of the reference state for a component is its solubility limit in the solution (melt) as there all the necessary conditions are being held. When the temperature, pressure or other components concentration changes, this reference state also will change (exceptions are systems with full mutual solubility), and this has to be taken into account.

4. In complex metallurgical system, it is more practical to calculate derivative of chemical potential from the integral Gibbs energy and derive activity from that, rather than do opposite. This could ensure that the artificial selection of the reference state would not violate thermodynamic rules.

## References

1. Schuhman, R.Jr. (1955) Application of Gibbs-Duhem equations to ternary systems. *Acta Metall*., **3**, 219–226.
2. Lupis, C.H.P. (1983) *Chemical thermodynamics of materials*. NY, North-Holland.
3. Kubaschewski, O., Alcock, C.B. (1979) *Metallurgical thermochemistry*. 5th Ed. Oxford, Pergamon Press.
4. Hillert, M. (1998) *Phase equilibria, phase diagrams and phase transformations: Their thermodynamic basis*. Cambridge, Cambridge Univ. Press., UK.
5. Lokkiluoto, A., Gasik, M. (2012) Activities and free energy of mixing of sulfuric acid solutions by Gibbs–Duhem equation integration. *J. Chem. Eng. Data*, **57**, 1665–1671.
6. Gasik, M. (2013) *Handbook of ferroalloys: Theory and technology*. Oxford, Elsevier/Butterworth-Heinemann, UK.
7. Okamoto, H., Massalski, T.B. (1991) Thermodynamically impossible phase diagrams. *J. Phase Equilib*., 12(**2**), 148–168.
8. Miettinen, J., Visuri, V.V., Fabritius, T. (2019) Thermodynamic description of the Fe–Al–Mn–Si–C system for modelling solidification of steels. *Acta Univ. Oul*., **C704**.
9. Ohtani, H., Hasebe, M., Nishizawa, T. (1984) Calculation of Fe–C, Co–C and Ni–C phase diagrams. *Transact. ISIJ*, **84**, 857–864.


## ХІМІЧНІ ПОТЕНЦІАЛИ І АКТИВНОСТІ У МЕТАЛУРГІЙНИХ ПРОЦЕСАХ


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Розглянуто процедуру коректного розрахунку хімічних потенціалів компонентів металургійних процесів і наведено важливість правильного вибору порівняльного стану. Цей вибір має вирішальне значення для адекватного визначення і розрахунку активності, що має відповідати принципам термодинаміки та бути раціональною для практичного застосування у піро- і гідрометалургійних технологіях. Бібліогр. 9, рис. 1.



*Ключові слова: термодинаміка; енергія Гіббса; хімічний потенціал; розчин; активність; розплав*

Надійшла до редакції 11.11.2020

**Wire and Tube: terms for 2022 are set**

After the cancellation of the leading international trade fairs Wire and Tube 2020 due to the current COVID-19 infection situation, the next editions will take place from May 9 to 13, 2022.

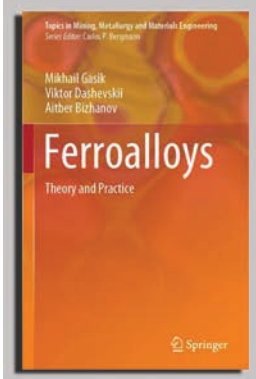
«We look forward to welcoming exhibitors and visitors to Düsseldorf in person again», says Daniel Ryfisch, Project Director Wire/Tube & Flow Technologies. «Corona has shown that digitalization brings many advantages. But it cannot replace personal meetings, conversations and contacts».

Wire and Tube, which were originally planned for March 30 to April 3, 2020, were on a record course until the COVID-19 related postponement. The number of registrations from exhibitors and visitors in spring exceeded all expectations. «For us this was a further signal and renewed confirmation that we have the No. 1 trade fairs for the wire, cable and tube industry here in Düsseldorf», explains Daniel Ryfisch. «This is where the international top decision-makers of the exhibitor and visitor sectors come together».

As usual, Wire will be located in halls 9 to 17 — and Tube in halls 1 to 7.0. Companies wishing to exhibit at Wire and Tube 2022 can already register starting at the end of March 2021. The official registration deadline is summer 2021, and the exact dates will be announced by Messe Düsseldorf at a later date.

www.wire-tradefair.com; www.tube-tradefair.com

**НОВА КНИГА**




Гасик М.І., Дашевскій В.Я., Біжанов А.М. **Феросплави: теорія та практика** / Під редакцією акад. НАНУ Гасика М.І. — Видавництво «Springer», Швейцарія, 2020 р. — 530 с.

У книзі систематизовано як базові аспекти теорії виробництва феросплавів (фізико-хімічні засади високотемпературних карбо-, сіліко- і алюмо-термічних процесів), так і практика технології отримання феросплавів з кремнієм, марганцем, хромом, молібденом, ванадієм, титаном, ніобієм, цирконієм, алюмінієм, лужноземельними і рідкоземельними металами, бором, нікелем, кобальтом, фосфором, селеном та телуром (включаючи характеристики шихтових матеріалів і технологічні параметри процесів). Розглянуто технології виробництва електродів і пічного обладнання для феросплавної промисловості, а також питання переробки відходів і методи вирішення екологічних задач у сучасному виробництві феросплавів.

Рекомендовано спеціалістам і науковцям, що працюють у галузі міжнародного феросплавного виробництва і технологій.

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