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Thermodynamic Models of Condensed Phases and Their Application in Materials Science

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Abstract

The review describes the main directions of thermodynamic modeling in materials science and gives a brief description of popular software products. The models used for the description of thermodynamic properties of pure substances and condensed solutions are presented. The regular solution model, which is used for multicomponent melts and disordered substitutional solid solutions, is described along with the Hillert-Staffanson model used for ordered substitutional solid solutions, intermetallics and interstitial phases. The use of the semi-empirical Miedema model for the estimation of the formation enthalpy of complex compounds, whose thermodynamic data are not available in literature, and for metastable (amorphous) phases is described. The method for calculating the excess entropy of mixing of amorphous phases is presented.

Keywords

Thermodynamic modeling; solution models; regular solution; Hillert-Staffanson model; semi-empirical Miedema model; excess entropy of mixing.

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Introduction

Thermodynamic modeling (**TM**) is widely used in modern materials science in the development of promising materials and methods for their production [1, 2]. It makes it possible to significantly reduce the amount of expensive experiments and to assess possible mechanisms of interaction. The main areas of TM can include the following:

1) calculation of the equilibrium composition of a multiphase multicomponent system for the production of new materials under isothermal conditions, for example, in reaction sintering, the interaction of solids with gases (oxidation, nitration), and metallic melts with slags, etc.;

2) calculation of the equilibrium composition and adiabatic temperature of the interaction of multicomponent systems in self-propagating high-temperature synthesis (SHS) of new materials;

3) construction of equilibrium diagrams of the state of binary and multicomponent systems.

Various software products are used in TM. For example, for the TM heterogeneous systems under different conditions (isobaric-isothermal, adiabatic, etc.) the ASTRA-4 program [3] and its Windows version of Terra [2] are used, for the calculation of SHS processes the specialized program ISMAN-THERMO [4] is used, for the calculation of phase equilibrium diagrams – expensive programs MTDATA, PANDAT, Thermo-Calc, etc. are used.

In modern TM methods, the CALPHAD approach (CALculation of Phase Diagrams) is used to describe the thermodynamic (**TD**) properties of phases (compounds and solid solutions based on pure components) [5, 6]. For disordered solid solutions of substitution and melts, a model of regular solutions is used [5], and for ordered solutions and implantation phases, the Hillert-Staffanson model [7, 8] is used. The semiempirical Miedema model is used to estimate the TD parameters of metastable phases (for example, amorphous phases) and multicomponent compounds, data for which are not available in the literature [9].

In this paper, the basic models of solutions are described and the ways of their use are shown for the TM synthesis of promising materials.

Thermodynamic properties of compounds

Traditionally, TD parameters of elements and compounds are described in the following form [10]:

$$C_p(T) = c_0 + c_1T + c_2T^2 + c_{-2}T^{-2} + c_{-3}T^{-3}, \quad (1)$$

$$H_T^0 = \Delta H_{298}^0 + \int_{298}^{T_{tr}} C_{p,s}(T)dT + \Delta H_{tr} + \int_{T_{tr}}^{T} C_{p,l}(T)dT; \quad (2)$$

$$S_T^0 = S_{298}^0 + \int_{298}^{T_{tr}} \frac{C_{p,s}(T)}{T}dT + \Delta S_{tr} + \int_{T_{tr}}^{T} \frac{C_{p,l}(T)}{T}dT;$$

$$\Delta S_{tr} = \Delta H_{tr}/T_{tr}; \quad (3)$$

$$G_T^0 = H_T^0 - TS_T^0, \quad (4)$$

whre C_p is heat capacity at constant pressure, T is тtemperature, H_T^0 is changes in the enthalpy in the formation of a given substance at temperature T, ΔH_{298}^0 and S_{298}^0 are standard enthalpy of substance formation at $T = 298$ K and its standard entropy, T_{tr} and ΔH_{tr} are temperature and enthalpy of phase transition (for example, melting), ΔS_{tr} is change in entropy during a phase transition, G_T^0 is change in Gibbs energy at temperature T; lower indices s and l denote a solid and liquid states.

Here, all the values are determined to 1 mole per formula unit, e.g., for the compound Ti_5Si_3, containing 5 moles of Ti and 3 moles of Si.

In the thermodynamic database (**TDBD**) of the ASTRA-4 and Terra programs, which are used for TM, the characteristics of the substances are specified in a different form. The enthalpy of H is the quantity

$$H(T) - H(T_0) = \int_{T_0}^{T} C_p(T)dT, \quad T_0 = 298 \text{ K}. \quad (5)$$

As the enthalpy, the "total enthalpy" I is used [2, 3]:

$$I = \Delta H_{298}^0 + H(T) - H(298), \quad (6)$$

and instead of G, the reduced Gibbs energy is used:

$$G^* = S - H/T, \quad (7)$$

which is connected with the "ordinary" Gibbs energy G by the formula

$$G = -TG^* + \Delta H_{298}^0 = I - TS, \quad (8)$$

and is approximated in the following form:

$$G^* = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_4 x + f_6 x^2 + f_7 x^3,$$
$$x = 10^{-4} T. \quad (9)$$

When using ASTRA-4 and Terra programs, if a compound is missing in the TDBD, it can be added there additionally. In this case, it is necessary to set the formula for the substance, the quantities ΔH_{298}^0 and S_{298}^0, and the coefficients appearing in the heat capacity expression (1), which must be found in the reference books. If the TD data for the substance are found in the works on the calculation of the phase diagrams by the CALPHAD method, they are usually given as the temperature dependence of the Gibbs energy $G(T)$. In this case, to determine the value ΔH_{298}^0, we must use the fundamental thermodynamic relations

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N_i};$$

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_{P,N_i}, \quad (10)$$

where P is pressure, N_i is the number of moles of the i-го substance.

Further, using the formulas (6) – (8), the resulting expression should be reduced to the form (9), whence it is possible to determine the parameters $f_1 - f_7$. Then in the TDBD the formula of the substance, the coefficients $f_1 - f_7$ and the value ΔH_{298}^0 are introduced.

The TM in ASTRA-4 and Terra programs make it is possible to set up to two regular condensed solutions, the TD parameters of which are entered by the user. The calculation of these parameters will be described below.

The model of regular solutions in the CALPHAD approach

In the framework of the CALPHAD-approach (CALculation of Phase Diagrams), all phases, including purely stoichiometric ones, are considered as solutions, and the TD functions are not determined for a formula unit, but for 1 mole of a solution (for example, not for Ti_5Si_3, but for $Ti_{5/8}Si_{3/8}$). For a liquid phase and disordered solid substitution solutions, where the atoms are located at lattice sites chaotically, a regular solution model is used [5, 6]:

$$G_\varphi = \sum_i x_i G_i^\varphi + G_{mix,id}^\varphi + G_{ex}^\varphi; \quad G_{ex}^\varphi \equiv H_{ex}^\varphi; \quad (11)$$

$$H_\varphi = \sum_i x_i H_i^\varphi + H_{ex}^\varphi, \quad (12)$$

where x_i is mole fraction of the i-th component, φ is phase designation, G_i^φ and H_i^φ are the Gibbs energy and the enthalpy of the i-th component in a given phase state, H_{ex}^φ is excess mixing enthalpy associated

with the interaction of components, $G^{\varphi}_{mix,id}$ is the ideal mixing energy (entropy term),

$$G^{\varphi}_{mix,id} = -TS_{id}, \quad S_{id} = -R\sum_i x_i \ln x_i , \qquad (13)$$

where R is universal gas constant, S_{id} is ideal, or configuration mixing entropy.

For multicomponent solutions, the excess mixing enthalpy is found as follows:

$$H^{\varphi}_{ex} = \sum_{i,j} x_i x_j L^{\varphi}_{ij} + \sum_{i,j,k} x_i x_j x_k L^{\varphi}_{ijk} + \sum_{i,j,k,l} x_i x_j x_k x_l L^{\varphi}_{ijkl},$$
$$i \neq j \neq k \neq l . \qquad (14)$$

Here L^{φ}_{ij}, L^{φ}_{ijk} и L^{φ}_{ijkl} are paired (*i–j*), triple (*i–j–k*) and quadruple (*i–j–k–l*) parameters of interaction of components in solution φ. Paired parameters are found using the Redlich-Kister-Muggian polynomials

$$L^{\varphi}_{ij} = \sum_n {}^{n}L^{\varphi}_{ij}\left(x_i - x_j\right)^n, \quad i \neq j, \quad n \geq 0 , \qquad (15)$$

and triple parameters are in the form

$$L^{\varphi}_{ijk} = {}^{0}L^{\varphi}_{ijk} + {}^{i}L^{\varphi}_{ijk} x_i + {}^{j}L^{\varphi}_{ijk} x_j + {}^{k}L^{\varphi}_{ijk} x_k,$$
$$i \neq j \neq k . \qquad (16)$$

For coefficients ${}^{n}L^{\varphi}_{ij}$, ${}^{m}L^{\varphi}_{ijk}$, $m \equiv 0, i, j, k,$ и L^{φ}_{ijkl}, $i \neq j \neq k \neq l$, a linear temperature dependence: $L = A + BT$ is usually used.

In the CALPHAD approach, the Gibbs energy of the *i*-th component G^{φ}_i in the phase state φ is determined in the following form:

$$G^{\varphi}_i = a_i + b_i T + c_i T \ln T +$$
$$+ \sum_n d_{i,n} T^n + H^{SER}_i + G^{\varphi}_{i,pres} + G^{\varphi}_{i,mag} . \qquad (17)$$

Here $G^{\varphi}_{i,pres}$ и $G^{\varphi}_{i,mag}$ are the quantities describing the contributions of pressure and magnetic ordering to the total Gibbs energy of the *i*-th element in the phase state φ, a_i, b_i, c_i и $d_{i,n}$ are numerical parameters, where n is integer, value $H^{SER}_i = H_i(T = 298) - H_i(T = 0)$ is correction for the transition from $T = 298$ K to $T = 0$ K as to the standard reference temperature of thermodynamic quantities.

The values of the parameters in expression (17) are given in the SGTE database (Scientific Group Thermodata Europe) [11] for all metallic and nonmetallic elements (with the exception of gases) in different phase states, including hypothetical ones.

The influence of pressure and magnetic ordering (ferromagnetic and paramagnetic) on the Gibbs energy is determined by the formulas [10]:

$$G_{pres} = AP\left(1 + a_0 T + a_1 T^2/2 + a_2 T^3/3 + a_3 T^{-1}\right); \qquad (18)$$

$$G_{mag} = RT \ln(B_0 + 1) g(\tau), \quad \tau = T/T^* ; \qquad (19)$$

$$g = \begin{cases} 1 - \left[\dfrac{79\tau^{-1}}{140p} + \dfrac{474}{497}\left(p^{-1} - 1\right) \times \right. \\ \left. \times \left(\tau^3/6 + \tau^9/135 + \tau^{15}/600\right)\right] \Big/ D \quad \text{при } \tau \leq 1, \\ -\left(\tau^{-5}/10 + \tau^{-15}/315 + \tau^{-25}/1500\right)/D \quad \text{при } \tau > 1, \end{cases}$$

$$D = 518/1125 + 11692\left(p^{-1} - 1\right)/15975. \qquad (20)$$

Here A and a_k, $k = 0$-3 are numerical parameters, which are given in the database SGTE, B_0 is average magnetic moment per atom, T^* corresponds to the Curie point T_C for ferromagnetic substances and the Néel point T_N for paramagnetic substances, parameter $p = 0.40$ for bcc lattice and 0.28 for other lattices [10].

Other TD functions (enthalpy, entropy, heat capacity) of pure substances in the phase state φ can be found using formulas (10).

The chemical potential, or the partial molar free energy of the *i*-th component of the solution φ is found as follows

$$\mu^{\varphi}_i = \left.\frac{\partial G_{\varphi}}{\partial N_i}\right|_{p,T,N_j,j\neq i} , \qquad (21)$$

and for a substitution solution or a melt is usually expressed as

$$\mu^{\varphi}_i = \mu^{0,\varphi}_i + \Delta h^{\varphi}_{ex,i} + RT \ln x_i , \qquad (22)$$

where $\mu^{0,\varphi}_i$ is the standard value of the chemical potential of the *i*-th component of the solution, $\Delta h^{\varphi}_{ex,i}$ is excess partial enthalpy of mixing; for the pure component, i.e. if $x_i = 1$, its chemical potential coincides with the Gibbs energy in a given phase state: $\mu^{0,\varphi}_i = G^{\varphi}_i$.

Since in formulas (11) – (16) the integral TD values (G and H) are expressed in terms of mole fractions x_i, rather than the number of moles N_i, then the partial molar quantities $z^{\varphi}_i \equiv \mu^{\varphi}_i, h^{\varphi}_i, \Delta h^{\varphi}_{ex,i}$ can be

determined from the following expression, in which the 1st component (solution base) is excluded,:

$$z_i^{\varphi} = Z_{\varphi} + \sum_{j=2}^{K} \left(\delta_{ij} - x_j\right) \frac{\partial Z_{\varphi}}{\partial x_j}, \qquad (23)$$

where δ_{ij} is the Kronecker symbol ($\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ if $i \neq j$), K is the number of components.

For the TM using ASTRA-r and Terra programs, taking into account the formation of a condensed solution, the coefficients of the polynomial describing the excess partial enthalpy of mixing components

$$\Delta h_{ex,i}^{\varphi} = \left(a + bT + cx_i + dTx_i\right)\left(1 - x_i\right)^2, \qquad (24)$$

where a, b, c и d are numerical parameters.

It is clear from the comparison of expressions (24) and (11), (12), (22) with allowance for (23) that the formula (24) used in these programs is correct only for binary solutions. For multicomponent solutions, it is approximate, since it does not take into account the pair and triple interaction of atoms of different varieties - otherwise the formula (24) would contain the concentrations of other components.

The Hillert-Staffanson Model

This model is used for compounds (carbides, nitrides, borides, etc.) and solid interstitial solutions, ordered solid substitution solutions and intermetallides, i.e. phases whose structure can be represented as two or more sublattices embedded in each other [7, 8]. The specific form of the model depends on the crystal structure of the phase, i.e. from the number of sublattices, and the possibility of placing atoms of a particular sort not only in "one's own", but also in the "alien" sublattice. As in the previous case, the Gibbs energy is found for 1 mole of the solution.

Consider a four-component phase $(A_{y'_A} B_{y'_B})_a \times \times (C_{y''_C} D_{y''_D})_b$ with two sublattices, where the atoms A and B are located in the first, and the atoms C and D – in the second sublattice; y_i', $i \equiv A, B$ and y_j'', $j \equiv C, D$ are the proportion of nodes in the first (′) and the second (″)sublattices occupied by atoms of a given kind (these quantities are used in place of atomic fractions x_i), $y_A' + y_B' = 1$, $y_C'' + y_D'' = 1$, $a + b = 1$. For such a phase, the model has the form [5–8]

$$G = G_{srf} + G_{mix,id} + H_{ex}, \quad H = H_{srf} + H_{ex}, \qquad (25)$$

where G_{srf} (surface of reference) and H_{srf} describe the free energy and enthalpy of the mixture of sublattices for the case when each of them is filled only by atoms of one kind, $G_{mix,id}$ is the ideal energy of mixing atoms in each of the sublattices, which is summed over all sublattices (this is the entropy term), H_{ex} is the excess enthalpy of mixing associated with the interaction of atoms belonging to different sublattices. Values G_{srf} and H_{srf} have the meaning of the "standard state" in relation to the situation when the phase is strictly stoichiometric and the excess mixing energy is absent ($H_{ex} = 0$).

The parameters in the formula (25) have the form

$$G_{srf} = y'_A y''_C G_{A:C} + y'_A y''_D G_{A:D} + \\ + y'_B y''_C G_{B:C} + y'_B y''_D G_{B:D};$$

$$H_{srf} = y'_A y''_C H_{A:C} + y'_A y''_D H_{A:D} + \\ + y'_B y''_C H_{B:C} + y'_B y''_D H_{B:D}. \qquad (26)$$

Here, values $G_{i:j}$ and $H_{i:j}$ have the meaning of the Gibbs energy and the enthalpy of the "pairwise" interaction between the 1st sublattice only filled with atoms i ($i \equiv A, B$), with a second sublattice filled only with atoms j ($j \equiv C, D$). They are found as

$$G_{i:j} = f\left(G_i, G_j\right) + P; \quad H_{srf} = f\left(H_i, H_j\right) + P;$$

$$P = A + BT; \quad i, j \equiv A, B, C, D, \qquad (27)$$

where G_k and H_k are the Gibbs energy and the enthalpy of atoms k, $k \equiv A, B, C, D$, with a crystal lattice corresponding to their standard phase state at room temperature, P is the so-called "lattice stability parameter" describing the change in Gibbs energy (actually enthalpy) in the hypothetical phase transformation of a pure element from its stable state to a state with a lattice corresponding to a given compound.

Values $G_{mix,id}$ (entropy term) and H_{ex} have the form

$$G_{mix,id} = -TS_{id};$$

$$S_{id} = -R\left[a\left(y'_A \ln y'_A + y'_B \ln y'_B\right) + b\left(y''_C \ln y''_C + y''_D \ln y''_D\right)\right], \qquad (28)$$

$$H_{ex} = y'_A y''_C y''_D L_{A:C,D} + y'_B y''_C y''_D L_{B:C,D} + y'_A y'_B y''_C L_{A,B:C} + \\ + y'_A y'_B y''_D L_{A,B:D} + y'_A y'_B y''_C y''_D L_{A,B:C,D}. \qquad (29)$$

Here $L_{A:C,D}$ is enthalpy of the "triple" interaction of atoms A located in the 1st sublattice with the second sublattice containing atoms C and D; $L_{A,B:C}$ is the energy of the "triple" interaction of atoms C located in

the second sublatticed with the first sublattice containing atoms A and B. Value $L_{B:C,D}$ is similar to $L_{A:C,D}$, while $L_{A,B:D}$ is similar to $L_{A,B:C}$; parameter $L_{A,B:C,D}$ has the meaning of the energy of the "quadruple" interaction of atoms A and B in the first sublattice with atoms C and D in the second sublattice. The following form of the record of the lower indices is used: the comma separates the atoms that are in the same sublattice, and the colon separates the sublattices themselves.

The parameters of the "triple" interaction are determined by the Redlich-Kister-Mugian polynomial (15), which in this model is written in terms of the values y' and y''. Thus, the expression for $L_{A,B:C}$ has the form

$$L_{A,B:C} = \sum_n {}^n L_{A,B:C}\left(y'_A - y'_B\right)^n, \quad n \geq 0, \qquad (30)$$

and the parameter of the "quadruple" interaction is described by the formula

$$L_{A,B:C,D} = {}^0L_{A,B:C,D} + {}^1L_{A,B:C,D}\left(y'_A - y'_B\right) + \\ + {}^2L_{A,B:C,D}\left(y''_C - y''_D\right). \qquad (31)$$

The four-component phase model with two sublattices (25) – (31) is written in a general form. For binary compounds, it has a simpler form and is related to the phase structure.

The Miedema's Semi-Empirical Model

It is used in the evaluation of TD parameters of complex compounds for which there is no data in the literature, as well as metastable (crystalline and amorphous) phases. The enthalpy changes when a phase is formed from components in a given phase state, i.e. excess enthalpy of mixing, is found as

$$H_{ex} = \Delta H^{chem} + \Delta H^{el}, \qquad (32)$$

where ΔH^{chem} is associated with the chemical interaction, and ΔH^{el} – with elastic interaction of atoms.

In the Miedema's model, the quantity ΔH^{el} exists only for solid crystalline phases, and ΔH^{chem} exists for any phases [9]. However, the calculations performed by the author for various compounds showed that taking into account the parameter H^{el} leads to a significant deviation of the value H_{ex} from experimental data and predictions of other models. Therefore in most cases this quantity is not taken into account.

The value of ΔH^{chem} is calculated by the formula

$$\Delta H^{chem} = \sum_{j>i=1}^{K} x_i x_j \left(x_j^s \Delta H_{i\,in\,j}^{chem} + x_i^s \Delta H_{j\,in\,i}^{chem}\right) f_{ij}. \qquad (33)$$

Here, x_i is molar concentration of i-th component, x_i^s is the concentration of atoms of the i-th type at the boundary of the Wigner-Seitz cells $\Delta H_{i\,in\,j}^{chem}$ is enthalpy of dissolution of the element i in j, $i \neq j$, the parameter f_{ij} has the form

$$f_{ij} = 1 + \gamma\left(x_i^s + x_j^s\right)^2, \qquad (34)$$

where $\gamma = 5$ for the amorphous phase, 0 for disordered solid solutions and 8 for ordered phases (solid solutions and intermetallides) [12].

Values x_i^s and x_j^s for each pair i–j are found by the formula

$$x_i^s = x_i V_i^{2/3} \Big/ \left(x_i V_i^{2/3} + x_j V_j^{2/3}\right), \quad x_j^s = 1 - x_i^s, \qquad (35)$$

where V_i is molar volume of the i-th element, which for some substances is corrected taking into account the type of crystal lattice [13].

Quantities $\Delta H_{i\,in\,j}^{chem}$ which are expressed in eV, are found as [13, 14]

$$\Delta H_{i\,in\,j}^{chem} = \frac{2P_{ij}V_i^{2/3}}{n_i^{-1/3} + n_j^{-1/3}} \times \\ \times \left[-\left(\varphi_i^* - \varphi_j^*\right)^2 e + \frac{Q}{P_{ij}}\left(n_i^{1/3} - n_j^{1/3}\right)^2 - \frac{R}{P_{ij}}\right], \qquad (36)$$

where e is elementary electric charge, φ_i^* is the electronegativity parameter for the i-th component, n_i is electron density parameter at the Wigner-Seitz cell boundary, P_{ij} and R/P_{ij} are numerical parameters that depend on the nature of the pair of elements i–j, value of $Q/P_{ij} = 9.4$ for all substances. Parameter values for various phase components are given in the works [9, 13, 14].

The Miedema's model uses specific dimensions, which are given here in the English notation: $[V_i] = \text{cm}^3$, $[R/P_{ij}] = \text{V}^2\text{e}$, $[n_i] = \text{d.u.}$, $[\varphi_i^*] = \text{V}$, $[Q/P_{ij}] = \text{V}^2\text{e(d.u.)}^{-2/3}$, $[P_{ij}] = \text{V}^{-1}\text{cm}^{-2}\text{(d.u.)}^{-1/3}$, where V ≡ Volt, e is electron charge, cm ≡ centimeter, d.u. (density unit) ≈ $6 \cdot 10^{22}$ cm^{-3} is electron density unit. Then in formula (36) the factor e is written only for the balance of dimensions, i.e., $e = 1$.

In amorphous phases, along with the ideal entropy of mixing S_{id} (see formula (13)), there is excess entropy S_σ, associated with the difference in atomic dimensions [15, 16]:

$$S_\sigma = R\left\{\frac{3}{2}\left(\zeta^2-1\right)y_1+\frac{3}{2}(\zeta-1)^2 y_2 - \right.$$
$$\left. -\left[\frac{1}{2}(\zeta-1)(\zeta-3)+\ln\zeta\right](1-y_3)\right\}, \qquad (37)$$

where $\zeta = 1/(1-\xi)$, $\xi = 0.64$ is packing factor for dense chaotic packing of spherical particles, and the parameters y_1, y_2 are y_3 are calculated as

$$y_1 = \frac{1}{\sigma_3}\sum_{j\geq i=1}^{K}(d_i+d_j)(d_i-d_j)^2 x_i x_j;$$
$$y_2 = \frac{\sigma_2}{\sigma_3^2}\sum_{j\geq i=1}^{K} d_i d_j (d_i-d_j)^2 x_i x_j; \qquad (38)$$
$$y_3 = \frac{\sigma_2^3}{\sigma_3^2}, \quad \sigma_n = \sum_{i=1}^{K} x_i d_i^n, \quad n = 2,3.$$

Here d_i and d_j are diameters of atoms of the i-th and j-th elements, $i \neq j$ (Goldschmidt diameters are usually used).

The application of the above solution models for TM expands the fields of application of TM, increases the accuracy of calculations and clarifies their physical meaning, which can be used in constructing more complex physicochemical models for the synthesis of new materials.

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