

Impurities distribution at phase transformations from ideal mixing phase

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General approach to consideration of impurities distribution at phase transformation from phase with ideal mixing is offered. It is based on using the equations of distillation refining with substitution of corresponding coefficients of distribution.

Предлагается обобщённый подход к рассмотрению распределения примесей при фазовых превращениях из фазы с идеальным перемешиванием, основанный на применении уравнений дистилляционного рафинирования при подстановке в них соответствующего коэффициента межфазового распределения.

As it is known a distribution of impurities between equilibrium phases is used in technologies of obtaining high pure materials, in particular in crystallization and distillation refining. The equilibrium between crystal and liquid is used under crystallization, while the equilibrium between liquid and gas is used under distillation refining. The theory of these processes has been developed and large scope of related experimental data has been accumulated [1–9]. The parameter that describes the concentration of impurity in phases that are in equilibrium is coefficient of interphase distribution K . The coefficient is calculated as ratio of concentrations of components in phases:

$$K = \frac{C'_A}{C'_B} / \frac{C_A}{C_B},$$

where C_A and C'_A are concentrations of component A in the first and second phases correspondingly at the phase equilibrium; C_B and C'_B are the same values for component B .

Or:

$$K = \frac{C_2}{1 - C_2} / \frac{C_1}{1 - C_1},$$

where C_1 and C_2 are concentrations of impurity in the first and second phases correspondingly at the phase equilibrium. It should be noted that K depends on conditions of the phase equilibrium.

Historically, crystallization and distillation methods of substances division were developed independently one from another that was reflected in separate publication of monographs related to these different methods or in separate description of the methods in different chapters of such monographs. In the literature equations describing these two methods are different and even coefficients of interphase distribution for the two processes have special names: distribution efficient k for crystallization process and separation factor α for distillation process.

Recently it was noticed that crystallization and distillation refining can be described by similar equations — with substitution in equations of corresponding coefficient of interphase distribution k at crystallization and α at distillation [10–13]. On the basis of this similarity a new refining method has been developed — zone distillation method as distillatory analogue of zone recrystallization [14].

At the same time the distribution of impurities under other phase transformations may be considered too. Today the existence of 6 aggregate states of substance it is recognized: crystal, liquid crystal, liquid, gas, plasma and quantum-mechanical state — Bose-Einstein condensate. Many phase transformations start from the good mixing phase that leads to idea about a possibility of general approach development to describe these transformations. The aim of the current work was to develop the general mathematical description of the impurities distribution between phases under different phase transformations.

Let's consider in general a transformation of the first phase in the second one under conditions of ideal mixing in both phases. Derivation of equations of impurities distribution between such phases will not differ from derivation of known equations of distillation refining [1, 3, 4]. As a result the general equations may be presented as the following:

$$C_2/C_0 = \frac{1 - (1 - G_2/G_0)^K}{G_2/G_0}, \quad (1)$$

$$C_1/C_0 = (G_1/G_0)^{K-1}, \quad (2)$$

where C_0 is initial concentration of impurity, C_1 and C_2 are concentrations of impurity in the first and second phases, correspondently, G_0 is initial mass of material, G_1 and G_2 are masses of the first and second phases, correspondently; K is a coefficient of interphase distribution. (It should be noted that equations (1) and (2) were derivated in assumption of small concentration of impurity.) If the second phase is solid state and the moving of impurities in it is difficult the equation (1) gives averaged value of impurity concentration in solid phase [11, 12]. Processes with transition of matter in solid phase is realized usually with conduct solidification of matter and production of crystal with elongated form or solid condensate with elongated form (at conduct crystallisation of liquid [1–3, 6–9] or at distillation with condensate pulling [10, 13], correspondently). In the crystal or condensate the distribution of impurities along its length is described by equation:

$$C/C_0 = K(1 - x/L)^{K-1}, \quad (3)$$

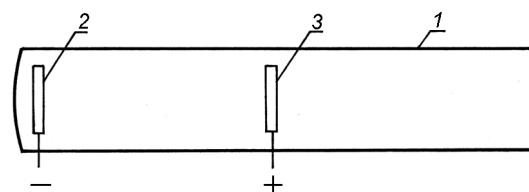


Fig. Scheme of the process with the phase transformation gas-plasma: 1 – container; 2 – electrode (catode); 3 – electrode (anode).

where C_0 is initial concentration of impurity, x is distance from the beginning of the crystal or condensate, L is length of it, C is concentration of impurity on distance equal x ; $K = k$ for crystallization processes [1, 3, 6–9] and $K = \alpha$ for distillation process [10, 13].

As an example of general approach to examination of impurities distribution at phase transformations let's consider the phase equilibrium gas-plasma. A possible scheme of device in which gas and plasma can be in phase equilibrium is shown on Fig. Gas is contained in chamber 1 with volume V . Part of chamber 1 is situated between electrodes 2 and 3. Under certain conditions (gas pressure and electrical voltage) in volume v between electrodes the plasma is formed while in the remainder of chamber 1 no ionized gas is contained. Since volume v is not separated hermetically from the residuary volume of chamber 1, plasma and gas are in dynamic equilibrium and redistribution of impurities between gas and plasma occurs.

Considering that densities of gas and plasma are equal let's transform equations (1) and (2) to more convenient form:

$$C_2/C_0 = \frac{1 - (1 - v/V)^K}{v/V},$$

$$C_1/C_0 = (V - v/V)^{K-1},$$

where C_0 is initial concentration of impurity, C_2 is concentration of impurity in plasma, C_1 is concentration of impurity in no ionized gas that is in equilibrium with plasma, v/V is volume part of plasma, $(V-v)/V$ is volume part of no ionized gas, K is a coefficient of interphase distribution at the phase equilibrium gas-plasma (K depends from conditions of equilibrium). Concentration of impurities in gas and in plasma is determined by volume parts of gas and plasma phases and by value of K coefficient. Impurities with $K > 1$ have

more probability to transfer to plasma while impurities with $0 < K < 1$ the most likely transfer to gas. The values of coefficient K for impurities at the phase equilibrium gas-plasma are not known. They may be determined experimentally for given conditions of the equilibrium. The task of calculation of these coefficients on known characteristics of components may be formulated.

Thus, equations (1)–(3) allow analyzing not only phase transitions liquid-crystal and liquid-gas but also other phase transformations. Using equations (1)–(3) phase transitions with participation of liquid crystals may be considered; equations (2) and (3) may be utilized in study of surface coating processes by plasma methods, and equations (1) and (2) may be useful in research of transformations related to quantum-mechanical phases (superfluid liquid, Bose-Einstein condensate). The distribution of impurities at transition from one crystal phase in other one can not be described by equations (1)–(3) because diffusion velocity of atoms in crystal phases is small.

Literature data about the values of interphase distribution coefficient in the first place related to the equilibrium crystal-liquid and in the second place to the equilibrium liquid-gas. For example the monograph [5] contains the values of coefficient k for 540 systems of elementary substances basis — impurity and the values of coefficient α for 70 systems (significant difference in quantities of values k and α perhaps connected with the different application of crystallization and distillation refining). Impurities distribution at other phase transformations either is not studied or there is scanty information. Thus, the purification of some liquid crystals (LC) by zone melting with estimation of distribution coefficient k is known (at number of known LC more than several hundred thousands) [15]. It should be noted that LC undergoes two phase transformation under the change from liquid to crystal state (liquid-LC and LC-crystal) and every transformation is characterized by own value of interphase distribution coefficient. The phase change liquid-gas can be used for improvement of LC distillation purification [16].

Thus, it is possible the general mathematical description of impurities distribution at phase transformations from phase with ideal mixing. This description is based on using the equations of distillation refining with substitution in the equations the corresponding values of distribution coefficient. Such approach can be effective for improvement existing technological processes with high-clean substances or for development new ones.

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References

1. G.G.Devyatykh, Yu.E.Elliev, Introduction to the Theory of Fine Purification of Substances, Nauka, Moscow (1981) [in Russian].
2. S.S.Gorelik, M.Ya.Dashevskiy, Material Science of Semiconductors and Dielectrics, Metallurgiya, Moscow (1988) [in Russian].
3. A.I.Belyayev, Physical and Chemical Foundations of Purification of Metals and Semiconductors, Metallurgiya, Moscow (1973) [in Russian].
4. A.I.Kravchenko, in: Probl. Nucl. Sci. Engineer., Ser. Nuclear Physics Investigations (Theory and Experiment) (1990), v.1, p.29.
5. L.A.Nisel'son, A.G.Yaroshevskii, Interphase Distribution Coefficients, Nauka, Moscow (1992) [in Russian].
6. A.Ya.Nashel'skii, V.I.Mevius, *Vysokochistyye Veshchestva*, **1**, 5 (1994).
7. Crystallization from Melts: Reference Issue, ed. I.Bartel, E.Burig, K.Hayn, L.Kuhard, Metallurgiya, Moscow (1987) [in Russian].
8. R.A.Laudise, The Growth of Single Crystals, Prentice-hall Inc., Englewood Cliffs, New Jersey (1970).
9. W.G.Pfan, Zone Melting, J.Willey and Sons, Inc., New York, London, Sydney (1966).
10. A.I.Kravchenko, *Inorgan. Mater.*, **43**, 916 (2007).
11. A.I.Kravchenko, *Funct. Mater.*, **16**, 101 (2009).
12. A.I.Kravchenko, *Inorgan. Mater.*, **46**, 91 (2010).
13. A.I.Kravchenko, in: Probl. Nucl. Sci. Engineer., Ser. Vacuum, Pure Materials, Superconductors (2008), v.1, p.18.
14. A.I.Kravchenko, Pat. Ukraine 47601, (2010).
15. V.A.Molochko, S.V.Krynkin, Z.A.Chernaya, R.A.Lidin, *Vysokochistyye Veshchestva*, **5**, 141 (1987).
16. A.I.Kravchenko, Pat. Ukraine 58356 (2011).

Щодо розподілу домішок при фазових перетворюваннях з фази з ідеальним перемішуванням

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Пропонується узагальний підхід до розгляду розподілу домішок при фазових переходах з фази з ідеальним перемішуванням, який заснований на застосуванні рівнянь дистиляційного рафінування при підстановці в них відповідного коефіцієнту міжфазового розподілу.