

## ABOUT MATERIAL EQUILIBRIUM

Prof. Etkin V.A.

It is shown, that change of image of heat and work in open systems entails necessity to revise of conditions of material equilibrium, found by Gibbs. Thus the chemical potential gives way to other potentials in conformity with conditions of unambiguity of researched processes.

**Introduction.** In the well-known work «About equilibrium of heterogeneous substances» [1] J. Gibbs first distributed methods of thermodynamics to open systems. The generalized equation of 1-st and 2-nd laws of thermodynamics of open systems (received in the further name of a Gibbs ratio), looked like:

$$dU = TdS - pdV + \sum_k \mu_k dN_k, \quad (1)$$

where  $U$  – internal energy of system;  $T, p$  - absolute temperature and pressure;  $\mu_k \equiv (\partial U / \partial N_k)$ - potential of  $k$ -th component (further named as chemical potential), found in conditions of a constancy of entropy of system  $S$ , its volume  $V$  and number of mole of other independent components  $N_m$ .

Being based on this equation, Gibbs has found conditions of equilibrium distribution of  $k$ -th substances in heterogeneous system which is not be located in external force fields. These conditions consist in equality of their chemical potential  $\mu_k$  in all parts of such system at presence in it of thermal and mechanical equilibrium.

However, as shows experience, the thermal, mechanical and material equilibrium comes generally not simultaneously. Thus for maintenance of material equilibrium (i.e. discontinuance of processes of redistribution of  $k$ -th substances) the presence of thermal and mechanical equilibrium sometimes is not obligatory. This case is considered in the theory of irreversible processes (TIP) [2,3], which studies processes of carry of substance under action of gradients or differences of temperature, pressure, electrical potentials etc.

According to this theory, the flow of  $k$ -th substance  $\mathbf{J}_k$  depends on all thermodynamic forces  $\mathbf{X}_j$ , acting in system and expressed (in their energy representation) through negative gradients or differences of temperatures, pressure and chemical potentials of all components of system [2,3]:

$$\mathbf{J}_k = \sum_j L_{kj} \mathbf{X}_j \quad (j=1,2,\dots,K, K+1, \dots,n), \quad (2)$$

where  $L_{kj}$  - empirical coefficients of transfer.

Thus in TIP the so-called stationary condition are considered, which are characterized by disappearance of flows of substance  $\mathbf{J}_k$  at preservation of flows of heat, charge etc. Stationary

conditions differ from a condition of material equilibrium by presence in stationary conditions alongside with thermodynamic parameters of coefficients of transfer  $L_{kj}$ .

Agrees to the phenomenological laws (2), the flows of  $k$ -th substances do not stop with the disappearance of falls or gradients of chemical potential of all components of system, i.e. with satisfaction of material equilibrium conditions on Gibbs. On the contrary, while there are flows of  $k$ -th substances, can be observed so-called heat-mass transfer (i.e. the transfer of internal energy by these substances), that corresponds to image about absence of thermal equilibrium. All this testifies to necessity of more precise definition of these conditions. You see is quite clear, that the laws (2) would obtain more simple "diagonal" form (with unique driving force  $\mathbf{X}_k$ ), if this force really corresponded to conditions of material equilibrium ( $\mathbf{J}_k = 0$  at  $\mathbf{X}_k = 0$ ).

**1. Conditions of independence of processes of heat exchange, volumetric deformation and mass transfer.** The necessity of reduction of the differential equations of researched processes in conformity with their conditions of unambiguity is well-known. With reference to a considered task it means, that if we want to allocate conditions of material equilibrium as independent from thermal and mechanical equilibrium, the energy of system  $U$  should be submitted through the variables really remaining independent in conditions of the considered problem.

Writing down a ratio (1), Gibbs assumed, that members  $TdS$  and  $pdV$  still (as well as in the closed systems) characterize heat exchange and work of expansion. It corresponded to existing in that time concepts of entropy  $S$  and volume  $V$  as physical magnitude, which constancy is a necessary and sufficient attribute of absence of processes of reversible heat exchange and work of expansion. Really, in [1] we find: «... if the system will consist of parts between which, as it is supposed, there is no thermal connection should be counted impossible any reduction of entropy in any of these parts as such changes cannot occur without carry of heat». However such statement is fair only for the closed systems. In open systems entropy  $S$  with necessity changes at change of common number of moles of system  $N$ . Therefore at definition of heat and work in open systems there was a necessity to exclude from complete change of entropy  $dS$  and volume  $dV$  that their part, which is caused which is caused by mass exchange and diffusion. Despite of available disagreements in a presence of this part [2,3], the majority of researchers has come to understanding of heat in open systems as that part of energy exchange which is not connected to transfer of substance through borders of system. Therefore we can not any more write instead of (1):

$$dU = dQ - dW + \sum_k \mu_k dN_k. \quad (3)$$

In open systems entropy  $S$  and volume  $V$  changes with necessity at change of common number of moles of system  $N$  (by mass transfer), and also at change of its composition (by diffusion). That circumstance breaks a condition of its constancy, underlying in above mentioned definition of chemical potential  $\mu_k$ . This remark concerns and to other definitions of chemical potential as derivative from enthalpy  $H$ , free energy  $F$  or Gibbs' potentials  $G$ . It is one more reason compelling to reconsider the material equilibrium conditions.

To mark out conditions of material equilibrium, it is necessary before all to determine the mass transfer as process which is not dependent on heat exchange and volumetric deformation, and last - as not dependent from mass transfer. For this purpose it be required knowledge of coordinates of processes of reversible heat exchange and works of expansion in open systems, i.e. parameters, with necessity varied at course of the mentioned processes, and remaining constant in their absence. To a regret, such coordinates till now are not found, as generates uncertainty of definition of heat and work in open systems [2,3]. It is obvious, that full entropy  $S$  and volume  $V$  of system are not such coordinates as they change and at mass transfer ( $N = \text{var}$ ). Are not them both specific entropy and volume of a mix  $s = \sum_k s_k r_k$ ,  $v = \sum_k v_k r_k$ , as they change at diffusion (change of molar portions  $r_k$  of  $k$ -th components at  $N = \text{const}$ ). Cannot be coordinates of heat exchange and work in open systems and partial molar values of entropy and volume of  $k$ -th components  $s_k$  and  $v_k$ , as they also change with change of composition of system.

For overcoming the specified difficulties we shall take into account change of entropy and volume of system in process of mixing, having presented them as:

$$S = \sum_k N_k s_{ko} + \Delta S_{mix}; V = \sum_k N_k v_{ko} + \Delta V_{mix}, \quad (4)$$

where  $s_{ko}(p, T)$  и  $v_{ko}(p, T)$  - molar entropy and volume of the pure  $k$ -th substances, of which the mix is made (considered as function of temperature  $T$  and pressure  $p$ );  $\Delta S_{mix}$ ,  $\Delta V_{mix}$  - change of entropy and volume in process of isobaric - isothermal mixing.

According to (2), full change of entropy and volume of a mix can be presented as the sum of reversible  $d_e S = \sum_k d(N_k s_k)$ ,  $d_e V = \sum_k d(N_k v_k)$  and irreversible ( $d_i S = dS_{mix}$ ,  $d_i V = dV_{mix}$ ) parts. In that case for definition of elementary heat  $\Sigma Q$  and elementary work of expansion  $\delta W$  in open systems it is necessary to deduct from full change of entropy  $dS$  and volume  $dV$  not only their that part  $\sum_k s_{ko} dN_k$  and  $\sum_k v_{ko} dN_k$ , which is caused by transfer of  $k$ -th components through borders of system, but also spontaneous changes  $dS_{mix}$ ,  $dV_{mix}$  in process of mixing:

$$dQ = TdS - TdS_{mix} - \sum_k T s_{ko} dN_k = Td_e S - \sum_k T s_{ko} dN_k; \quad (5)$$

$$dW = pdV - pdV_{mix} - \sum_k p v_{ko} dN_k = pd_e V - \sum_k p v_{ko} dN_k. \quad (6)$$

As in reversible processes  $d_e S - \sum_k s_k dN_k = \sum_k N_k ds_k$  and  $d_e V - \sum_k v_k dN_k = \sum_k N_k dv_k$ , the given definition of heat and work is equivalent to expression of heat and work in the closed system consisting of same  $k$ -th noninteracting substances (or substances separated from each other with mobile heat-conducting partition):

$$\bar{d}Q = \sum_k N_k T ds_{ko}; \quad \bar{d}W = \sum_k N_k p dv_{ko}. \quad (7)$$

Thus, in open multicomponent systems as coordinates of heat exchange and work of expansion it can be accepted the molar entropy  $s_{ko}$  and molar volumes  $v_{ko}$  of any of components of the reversible prepared mixture. The finding of these coordinates obviate difficulties in definition of heat and work for open systems [2,3], allowing to present full differential of internal energy  $U$  as function of really independent variables  $s_{ko}$ ,  $v_{ko}$  and  $N_k$ :

$$dU = \sum_k N_k T ds_{ko} - \sum_k N_k p dv_{ko} + \sum_k \zeta_k dN_k, \quad (8)$$

where  $\zeta_k$  – diffusion potential of  $k$ -th component, found in conditions of a constancy of  $s_{ko}$ ,  $v_{ko}$  and  $N_m$ .

The expression (8) represents the alternative form of ratio (1), in which right part really correspond to elementary quantities of heat exchange  $\bar{d}Q$ , works of expansion  $\bar{d}W$  and energy mass transfer  $\bar{d}U_m$ :

$$dU = \bar{d}Q - \bar{d}W + \sum_k \zeta_k dN_k. \quad (9)$$

**2. Communication of the diffusion and chemical potentials.** Let's subtract from first two composed expressions (1) members  $\sum_k s_k dN_k$ ,  $\sum_k v_k dN_k$  and simultaneously we add them to it last composed to not break balance of energy. Taking into account, that the ratio (1) concerns to reversible processes ( $dS = d_e S$ ,  $dV = d_e V$ ), and comparing expression received after such rearrangement composed, with (8), we shall find:

$$\bar{d}U_m = \sum_k \zeta_k dN_k = \sum_k (\mu_k + Ts_{ko} - pv_{ko})dN_k, \quad (10)$$

From here follows, that

$$\zeta_k = \mu_k + Ts_{ko} - pv_{ko}. \quad (11)$$

If to take advantage of known representation of chemical potential  $\mu_k$  through partial molar quantities (partial molar energy  $u_k$ , partial molar entropy  $s_k$  and partial molar volume  $v_k$  of  $k$ -th component  $\mu_k = u_k - Ts_k + pv_k$  [2,3] the ratio (9) can give a kind:

$$\zeta_k = u_k + T(s_{ko} - s_k) - p(v_{ko} - v_k) . \quad (12)$$

The difference  $s_k^* \equiv (s_{ko} - s_k)$  between entropy  $s_{ko}$ , which one mole of  $k$ -th substances has import in system, and the valid increment of mixes entropy  $s_k$  in isobaric-isothermal process of its input and the subsequent mixture, has been considered for the first time by E. Eastman (1926) and C. Wagner (1929 [2,3]). They have named  $s_k^*$  as "entropy of transfer", and corresponding to it heat

$$q_k^* \equiv Ts_k^* = T(s_{ko} - s_k) \quad (13)$$

as «heat of transfer» of  $k$ -th component (In the literature there are also other definitions of the given value. So, Haase [3] names value  $s_k$  as "entropy of transfer". We adhere to most customary definitions [2], understanding (after Eastman) under entropy of transfer the value  $s_k^* = q_k^*/T$ ). In the theory of irreversible processes the values  $s_k^*$  is entered as one coefficients of transfer  $L_{kj}$  and treated as energy, transported by mole of  $k$ -th substances in absence of a gradient of temperature. Now after its representation through parameters of a state it appears as the thermodynamic function having sense of heat of mixture.

By analogy size

$$w_k^* = p(v_{ko} - v_k) \quad (14)$$

it would be possible to name as "work of transfer". Difference  $(v_{ko} - v_k)$  characterizes the volumetric effects connected to input of  $k$ -th substance and caused by interaction of components during mixture. In specific case of phase transitions  $q_k^*$  and  $w_k^*$  get sense of heat and work of these transitions.

For not interacting substances ( $q_k^*, w_k^* = 0; u_k = u_{ko}$ ) potential  $\zeta_k$  is equal to internal energy  $u_{ko}$ , transported by mole of  $k$ -th substance through borders of system. It is easy to be convinced of it, reasoning "from opposite". Really, for pure of  $k$ -th substance as a closed system is fairly the expression  $du_{ko} = \delta q_k - \delta w_k = Tds_{ko} - pdv_{ko}$ . Multiplying all members of this equality on  $N_k$  and taking into account, what  $\delta Q = \sum_k N_k \delta q_k$ ;  $\delta W = \sum_k N_k \delta w_k$ , after Legendr's transformation  $N_k du_{ko} = dU - u_{ko} dN_k$  and summation on all components, for a mix of not interacting substances we have:

$$dU = \delta Q - \delta W + \sum_k u_{ko} dN_k. \quad (15)$$

It is easy to see, that the equation (3) does not pass in (15) in absence of interaction of components, as that should be expected. It is one more argument showing of necessity of replacement of chemical potential on diffusive.

That circumstance, that heat and work of transfer excluded from  $dQ$  and  $dW$ , have come in other part of the equation of balance of energy (1)  $dU_m$ , quite naturally, as the balance of energy thus should not be broken. Nevertheless such regrouping of the members predetermines in the further transition of conditions of stationarity in conditions of equilibrium. It is connected that diffusion potential, remaining function of a condition, takes into account thermal and volumetric effects, which in TIP concern to functions of process.

**3. Conditions of material equilibrium of heterogeneous systems.** Let's find out now conditions of equilibrium distribution of  $k$ -th component following from ratio (8) and (9). Applying Gibbs's method, we shall break system into a number of homogeneous subsystems, for each of which is fair the ratio (8). Designating parameters concerning to these subsystems according to one, two, etc. strokes, we have:

$$dU = \sum_k N_k' T' ds_{ko}' - \sum_k N_k' p' dv_{ko}' + \sum_k \zeta_k' dN_k' + \\ + \sum_k N_k'' T'' ds_{ko}'' - \sum_k N_k'' p'' dv_{ko}'' + \sum_k \zeta_k'' dN_k'' + \dots = 0. \quad (16)$$

This expression should satisfy to the equations of the imposed connections, which reflect a constancy  $N_k$  in system as a whole at an exchange by  $k$ -th substance between its parts and invariance of parameters  $s_{ko}'$ ,  $s_{ko}''$ ,  $v_{ko}'$  and  $v_{ko}''$  by thus:

$$dN_k' + dN_k'' + \dots = 0 \quad (k = 1, 2, \dots, K). \quad (17)$$

$$ds_{ko}' = ds_{ko}'' = dv_{ko}' = dv_{ko}'' = 0; \quad (18)$$

Comparing expressions (16...18), we come to a conclusion, that for diffusion equilibrium in conditions  $s_{ko}$ ,  $v_{ko} = \text{const}$  ( $p$ ,  $T = \text{const}$ ) it is necessary and enough:

$$\zeta_k' = \zeta_k'' = \zeta_k^d. \quad (19)$$

Thus, the known statement that by a condition of equilibrium distribution of the any real component is a constancy of its potential in all parts of system, remains in valid – it is changes only the form of representation of this potential. However now becomes completely clear, that potential of a component changes depending on conditions of unambiguity of researched process. Let's assume, that the subsystems have a rigid environment and separated from each

other by partition, permeable for solvent. Then the input of this substance is accompanied by infringement of mechanical equilibrium. It is connected with so-called "work of input"  $p v_k dN_k$  and work of transfer  $p(v_{ko} - v_k)$ , creating in common pressure differential  $\Delta p = p'' - p'$  between parts of system. For such a case equations of the imposed connections accept a kind:

$$dN_k' + dN_k'' + \dots = 0 ; \quad (20)$$

$$dV' = dV'' = \dots = 0 ; \quad (21)$$

$$ds_{ko}' = ds_{ko}'' = \dots = 0 ; \quad (22)$$

In these conditions, characteristic for osmosis, independent variables are  $s_{ko}$ ,  $V$  and  $N_m$ . Resulting the ratio (1) in conformity with conditions of unambiguity (20...22) and believing in (1)  $dV = 0$ , after a regrouping its composed (subtraction and addition of the member  $\sum_k T s_k dN_k$  we have:

$$dU = \sum_k N_k T ds_{ko} + \sum_k \zeta_k dN_k . \quad (23)$$

where

$$\zeta_k = h_k + T(s_{ko} - s_k), \quad (24)$$

$h_k$  – partial molar enthalpy of  $k$ -th component.

This potential is named in [6] osmotic. In a case of osmotic equilibrium:

$$\zeta_k' = \zeta_k'' \quad (25)$$

In an even more special case, when the components do not interacting ( $s_{ko} = s_k$ ,  $h_k = h_{ko}$ ), the condition (25) accepts a kind:

$$h_k' = h_k'' . \quad (26)$$

The infringement of this condition entails, for example, process of a filtration. On this basis it is possible to call enthalpy as filtration potential. Thus, a variety of conditions of unambiguity entails a variety of potential of a component.

**4. Discussion of results.** The specified form of potential of a component differ from chemical potential by independence of processes of heat exchange and expansion, simultaneously proceeding in system. It makes conditions of material equilibrium independent from conditions of thermal and mechanical equilibrium.

Further, due to replacement of chemical potential by diffusion it is possible to find that unique (resulting) driving force

$$\mathbf{X}_k = -\Delta\zeta_k = -\sum_k (\partial\zeta_k/\partial c_m) \Delta c_m - q_k^* \Delta T + w_k^* \Delta p, \quad (m=2,3,\dots,K) \quad (27)$$

which disappearance lead to discontinuance of process of transfer of  $k$ -th substance [5]. Thus the diffusion laws obtain more simple ("diagonal") form

$$\mathbf{J}_k = D_k \mathbf{X}_k, \quad (28)$$

in which the flow of  $k$ -th substance  $\mathbf{J}_k$  is defined by a negative gradient (or difference) of diffusion potential only  $k$ -th component  $\mathbf{X}_k$  as function of temperature  $T$ , pressure  $p$  and concentration  $c_m$  of all independent components of system. In comparison with expression (2) it reduces in  $K^2$  of time number of experimental coefficients of diffusion. Self-consistency of such description of diffusion processes is shown in [5,6].

Thirdly, the thermodynamic forces (28), found on the basis of the specified conditions of material equilibrium, take into account thermal and volumetric effects of mixture and consequently alongside with processes of diffusion and osmos describe the "collateral" phenomena, accompanying them [5,6]. Thus the specified effects receive a new explanation as a consequence of superposition of the components  $(\partial\zeta_k/\partial c_m)\Delta c_m$ ,  $q_k^* \Delta T$  and  $w_k^* \Delta p$  of a resulting force (28).

In – fourth, the more precise definition of material equilibrium conditions has allowed to offer a new method of research of irreversible processes, which due to preservation of the diagonal form of the generalized laws (28) does not require application of the Onsager's reciprocal relations and consequently is not limited to frameworks of the linear phenomenological laws [7]. The generality of this method is shown in [8] by reception of all thermomechanical, thermochemical, thermoelectrical and so on effects, considered usually in the theory of irreversible processes. All this it confirms utility of the undertaken specification of material equilibrium conditions.

## REFERENCES

1. *Gibbs J.W.* The Collected Works. Thermodynamics. New York: Longmans, Green and Co., 1928. V. 1.
2. *Groot S.R., Mazur P.* Non-equilibrium Thermodynamics, Amsterdam, 1962.
3. *Haase R.* Thermodynamics of Irreversible Processes, Darmstadt, 1963
4. *Etkin V.A.* Russian Journal of Physical Chemistry, **63**, No.6, 918-919 (1989). [English translation Zh. Fiz. Khim., **63**, No.6, 1660-1662(1989)].



5. *Etkin V.A.* Russian Journal of Physical Chemistry, **68**, No.12, 518-522 (1994). [English translation Zh. Fiz. Khim., **68**, No.12, 2117-2121(1994)].
6. *Etkin V.A.* Journal of Eng. Physics and Thermophysics, **72**, No.4, 748-754 (2000) [English translation Eng.-Phys. J. ,**72** , No.1, 776-782 (1999)].
7. *Etkin V.A.* Russian Journal of Physical Chemistry, **65**, No. 3, 339-343 (1991). [English translation Zh. Fiz. Khim., **65**, No.3, 642-651(1991)].
8. *Etkin V.A.* Thermokinetics (Thermodynamics of non-equilibrium processes of energy transfer and energy transformation) [in Russian] – Togliatti (1999).

D-r Sc., prof. Etkin V.A.  
 Geula Str., 33197, Haifa, Israel,  
 Tel. (972-4)-8622688, E-mail: v\_a\_etkin@bezeqint.net

### NOTATION

$U, S, V$  – internal energy, entropy and volume of the system;  $N_k, N$  – number of moles of  $k$ -th substances and systems as a whole;  $dQ, dW, dU_m$  – elementary amounts of heat, work and the energy transferred by substance,  $J$ ;  $T, p$  – absolute temperature (K) and pressure, Pa;  $u, h$  – its specific internal energy and enthalpy,  $J/kg$ ;  $v$  – specific volume of the system,  $m^3/kg$ ;  $s$  – its specific entropy,  $J/kg \cdot K$ ;  $v_k, s_k$  – partial molar volume ( $m^3/mole$ ) and partial molar entropy ( $J/mole \cdot K$ ) of the  $k$ -th component;  $s_{ko}, v_{ko}$  – molar volume and entropy of pure  $k$ -th substances;  $\mu_k$  – chemical potential of a mole of the  $k$ -th component ( $J/mole$ );  $r_k, c_k$  – its molar and mass fraction (mole/mole and  $kg/kg$ );  $\zeta_k, \zeta_k$  – diffusion and osmotic potentials of a mole of the  $k$ -th component,  $J/mole$ ;  $X_k$  – driving force of the process of his transfer;  $q^*, w^*$  – heat and work of transfer of the  $k$ -th substances,  $J/mole$ .