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ENERGY CHARACTERISTICS OF MASS TRANSFER IN POROUS SOLIDS

V. V. Beloborodov

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We obtained equations for the energy characteristics of the system "solid–liquid (vapor)" and its individual phases and for numerical values of the energy characteristics for various systems, including ones used in industry. Their analysis is performed and an assessment from the energy standpoint is given. The "mesobody" concept is introduced and described qualitatively.

The adopted characteristic of mass transfer in the system "solid–liquid" (extraction and adsorption from liquids) or "solid–vapor (gas)" (drying, humidification, and adsorption from a vapor or a gas) is the mass-transfer (diffusion) coefficient, which belongs to the kinetic quantities. At the same time, for analysis of mass transfer it is important to know the energy that must be expended on overcoming the resistance of the system "solid–liquid (vapor, gas)" and its individual phases (a solid, a liquid, a vapor, and a gas). As applied to a moist (water-containing) body as a whole (the system "solid–liquid, vapor"), this problem was addressed by Polanyi [1] and Rebinder [2]. As a result, the following well-known equation was obtained for the energy of moisture–solid binding:

$$W = - RT \ln \varphi \,, \tag{1}$$

where $\varphi = p_{\text{eq}}/p_{\text{s}}$.

Equation (1) can be extended to the processes of evaporation-condensation (desorption-sorption of vapor) of any liquid; however, it cannot be referred to the processes of mass transfer without evaporation (condensation), among which are, for example, extraction and adsorption from liquids.

For the system "porous solid–liquid," as is demonstrated in [3], the laws of diffusion for a liquid from its kinetic theory can be employed [4].

With account for the foregoing, using expressions for the diffusion coefficient from [4] it is possible to write

$$D_{\text{liq}} = \frac{\delta^2}{6\tau_0} \exp\left(- \frac{W'_{\text{liq}}}{kT}\right), \tag{2}$$

$$D_{\text{sol.liq}} = \frac{\delta^2}{6\tau_0} \exp\left(- \frac{W'_{\text{sol.liq}}}{kT}\right). \tag{3}$$

From Eqs. (2) and (3) we obtain

$$W'_{\text{sol}} = W'_{\text{sol.liq}} - W'_{\text{liq}} = - kT \ln \frac{D_{\text{sol.liq}}}{D_{\text{liq}}} \,. \tag{4}$$

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Physically, W'_{sol} is the energy that must be expended in order for one molecule of the material for a distance between holes in the liquid δ to overcome the resistance of the solid structure proper. This is not sufficient for diffusion. Energy is also needed for overcoming the resistance of the liquid proper W'_{liq}, i.e., overall, diffusion in the system "solid–liquid" requires the energy $W'_{\text{sol.liq}}$.

Diffusion of one mole of the material ($R = kN$) requires

$$W_{\text{sol}} = -RT \ln \frac{D_{\text{sol.liq}}}{D_{\text{liq}}}. \tag{5}$$

If W_{sol} is the energy for overcoming the resistance for a distance δ, then the energy for overcoming the resistance for the distance l (the body size) is

$$W_{\text{sol}l} = -\frac{l}{\delta} RT \ln \frac{D_{\text{sol.liq}}}{D_{\text{liq}}}. \tag{6}$$

Correspondingly, $W_{\text{liq}l} = (l/\delta)W_{\text{liq}}$, $W_{\text{sol.liq}l} = (l/\delta)W_{\text{sol.liq}}$, and $W_{\text{sol.sol}l} = (l/\delta)W_{\text{sol.sol}}$.

Calculated results for W_{sol}, W_{liq}, and $W_{\text{sol.liq}}$ are presented in Table 1. In accordance with [4], $\delta = 10^{-10}$ m and $\tau_0 = 10^{-13}$ sec. The values of D_{liq} for most solvents were taken from [5], those for trichloroethylene were obtained from the nomogram of Otmer and Takara [5], and W_{liq} for water was found approximately from [4]. The values of $D_{\text{sol.liq}}$, l, and T were taken from the references given in Table 1. The magnitudes of W_{liq} and $W_{\text{sol.liq}}$ were determined from Eqs. (2) and (3), respectively.

It should be noted that, in the diffusion of various metals, for example, copper, $W_{\text{sol.sol}}$ ranges from 58.9 kJ/mole (Au) to 117.0 kJ/mole (Pb) [4].

Analysis of Table 1 permits one to draw the following conclusions:

1. In terms of energy, the system "solid–liquid" occupies an intermediate position between the systems "solid–solid" and "liquid–liquid," which is quite natural. However, the range of $W_{\text{sol.liq}}$, depending on the porous structure of the solid, is wide: on the one hand, $W_{\text{sol.liq}}$ approaches $W_{\text{sol.sol}}$ (for example, 36.5 kJ/mole for crumbled sunflower–hexane and 58.9 kJ/mole for Au–Cu), and on the other hand, it approaches W_{liq} (for example, 11.8 kJ/mole for solid layer–water and 9.3 kJ/mole for simply water). It may well be that at the freezing temperature or below it, $W_{\text{sol.liq}}$ approaches $W_{\text{sol.sol}}$ even more for metals.

2. Present-day traditional technologies for preparation of materials for extraction do not change their internal structure very appreciably. This is seen, for example, from a comparison of W_{sol} for a soy kernel (an intact, native cellular structure) and a moist soy petal (structural disruption due to the flattening of kernel particles on special machines): in both cases, the magnitude of $W_{\text{sol}}/W_{\text{sol.liq}}$ amounts to 70%. The extraction is accelerated mainly due to a reduction in the particle size.

3. Under actual conditions, i.e., with the particle sizes used in practice, the energy characteristics in the considered cases increase by seven orders of magnitude ($l/\delta = 10^{-3}/10^{-10}$).

The generality of Eq. (5) and, correspondingly, the relations for W_{liq}, $W_{\text{sol.liq}}$, $W_{\text{sol}l}$, $W_{\text{liq}l}$, and $W_{\text{sol.liq}l}$ can be demonstrated, for example, by comparing the values of W_{sol} calculated from experiments on drying or distillation of a solvent and experiments on extraction. In the first case, W_{sol} was calculated from the equation (see Table 2)

$$W_{\text{sol}} = -RT \ln \frac{a_{\text{m}}}{D_{\text{v}}}. \tag{7}$$

In these calculations, $a_{\text{m}} = 1.09 \cdot 10^{-9}$ m^2/sec for a sunflower kernel in drying was taken from [14] as the mean of four values, $D_{\text{v}} = 4.06 \cdot 10^{-5}$ m^2/sec for the system "water vapor–air" at 373 K and $D_{\text{v}} = 3.1 \cdot 10^{-5}$ m^2/sec at 323 K were taken from [15], a_{m} for crumbled sunflower in drying was calculated from [16], the values of a_{m} for the system "solvent vapor–air" at 333 and 363 K were taken from [16], and the values of D_{v} for hexane in air were calculated from the Jilliland equation [17].

TABLE 1. Energy Characteristics of Various Systems

Solid phase	Liquid phase (solvent)	l, mm	T, K	W_{sol}, kJ/mole	W_{liq}, kJ/mole	$W_{sol.liq}$ kJ/mole	$\frac{W_{sol}}{W_{sol.liq}}$, %	Reference
Layer of solid spheres with structure:								
cubic	Water	15	281	2.5	9.3	11.8	21.2	[6]
rhombic tetragonal	"	15	281	3.1	9.3	12.4	25.0	[6]
unordered	"	15	281	3.4	9.3	12.7	26.8	[6]
rhombic triangular	"	15	281	3.6	9.3	12.9	27.9	[6]
octahedral	"	15	281	3.8	9.3	13.1	29.0	[6]
tetrahedral	"	15	281	4.2	9.3	13.5	31.1	[6]
Kernel of soy seeds	Extractive gasoline	2.90	293	19.5	8.1	27.6	70.6	[5]
		3.35	293	19.0	8.1	27.1	70.1	[5]
Kernel of peanut seeds	Same	4.3	293	13.8	7.6	21.4	64.4	[7, 8]
	"	4.3	309	14.5	7.5	22.0	65.9	[7, 8]
	"	4.3	325	16.2	7.4	23.6	68.8	[7, 8]
	"	4.3	341	16.3	7.3	23.6	69.2	[7, 8]
Microtome sections of peanut seeds	Technical hexane	0.10	298	17.3	7.8	25.1	69.1	[9]
	Same	0.13	298	17.3	7.8	25.1	69.1	[9]
	Same	0.16	298	17.6	7.8	25.4	69.4	[9]
	Same	0.20	298	18.9	7.8	26.7	70.8	[9]
Crumbled sunflower:								
without husks	Hexane	0.06	323	29.0	7.5	36.5	79.5	[10]
5% husks	"	0.07	323	26.6	7.5	34.1	78.0	[10]
10% husks	"	0.08	323	26.6	7.5	34.1	78.0	[10]
15% husks	"	0.10	323	26.1	7.5	33.6	77.7	[10]
25% husks	"	0.11	323	22.7	7.5	30.2	75.2	[10]
Moist soy petal	Extractive gasoline	0.18	328	20.7	7.8	28.5	72.6	[5]
		0.23	328	19.1	7.8	26.9	71.0	[5]
	Same	0.28	328	18.2	7.8	26.0	70.0	[5]
	"	0.33	328	18.8	7.8	26.6	70.7	[5]
	Dichloroethane	0.18	328	20.8	9.6	30.4	68.5	[5]
	"	0.23	328	15.6	9.6	25.2	62.0	[5]
	"	0.28	328	13.6	9.6	23.2	58.7	[5]
	"	0.33	328	13.0	9.6	22.6	57.6	[5]
	Extractive gasoline	0.11	325	21.1	7.8	28.9	73.1	[11]
	Same	0.11	325	21.7	7.8	29.5	73.7	[11]
	"	0.15	328	16.1	7.8	23.9	67.4	[5]
	Trichloroethylene	0.10	300	15.0	4.7	19.7	76.1	[12]
	"	0.14	300	15.2	4.7	19.9	76.4	[12]
	"	0.22	300	12.1	4.7	16.8	72.0	[12]
	"	0.27	300	13.5	4.7	18.2	74.2	[12]
Soy grit	Extractive gasoline	–	328	15.6	7.8	23.4	66.7	[13]
Grit of coriander waste	Same	0.38	328	19.7	7.8	27.5	71.7	[5]
Forepress sunflower petal	Hexane	–	323	17.7	7.5	25.2	70.3	[10]

TABLE 2. Magnitude of W_{sol} from Data on Drying (Distillation of the Solvent)

Material	W_{sol}, kJ/mole
Kernel (crumbled) of sunflower seeds	32.9 (kernel, drying)
Crumbled sunflower seeds with a husk content of, %	
0	21.7
5	18.2 (drying)
10	17.5
15	18.0
Forepress sunflower petal	22 20.7 19.6 (distillation of solvent-gasoline) 17.2

As is seen from a comparison of the data of Tables 1 and 2 for the corresponding materials, the energy assessment of the porous structure of a solid gives close magnitudes, regardless of the experimental data (on drying or extraction) from which the kinetic coefficients that enter into Eqs. (5) and (7) were obtained. Naturally, this can apply to cases where the process parameters proper (temperature, moisture content of the material, etc.) do not have a marked effect on the porous structure.

Equations (5) and (7) can be written in the generalized form

$$W_{\mathrm{sol}} = -RT \ln \psi , \tag{8}$$

where ψ is the ratio of the kinetic coefficient (of diffusion or moisture transfer) inside a solid to the corresponding kinetic coefficient in a free liquid or a free vapor.

Although identical in structure, relations (1) and (8) are fundamentally different.

In Eq. (1), the quantity φ is determined from data on equilibrium sorption (an equilibrium state), whereas in Eq. (8) the quantity ψ is obtained from data on the process kinetics (a nonequilibrium state). The quantity W characterizes the energy of various forms of moisture-solid binding; with increase in φ (the relative humidity of air), W decreases, and at $\varphi = 1$, $W = 0$. The quantity W_{sol} ($W_{\mathrm{sol}l}$) characterizes the energy needed to overcome the resistance of a solid to diffusion (moisture transfer), it is an energy characteristic of the porous structure of a solid and of the ability of a solid to confine the transferred material (hinder the material transfer). As ψ increases, W_{sol} decreases, and at $\psi = 1$, $W_{\mathrm{sol}} = 0$ (there is no porous body, or the pores (channels) are so large that $D_{\mathrm{sol.liq}} = D_{\mathrm{liq}}$ or $a_{\mathrm{m}} = D_{\mathrm{v}}$). Conversely, with decrease in ψ, W_{sol} increases, and when $\psi \to 0$, $W_{\mathrm{sol}} \to \infty$, i.e., diffusion (moisture transfer) does not occur at all. Such a body is thermodynamically inert relative to the given medium (a solvent or a material in the vapor phase). Generally, this is observed in the chemical interaction of a diffusing material with a solid material. A characteristic example is the so-called residual oil content, i.e., a certain content of lipids in the solid phase (grist) that are not extracted by the given solvent.

Other things being equal, a fundamental difference of W from W_{sol} ($W_{\mathrm{sol.liq}}$, etc.) is that W depends on the moisture content of the solid, whereas W_{sol} ($W_{\mathrm{sol.liq}}$, etc.) does not depend on the content of the extracted (sorbed) material in the solid, since it characterizes an invariable, under the given conditions, part of the system, which is the structure of the porous solid.

With decrease in the pore size in the systems "solid–liquid (vapor)," the structural resistance of the solid increases and at certain values of d that are comparable to δ, especially when $d \le \delta$, the internal mass transfer begins to follow the mechanism for both a liquid (vapor) and a solid crystal body. Here, a molecule of the diffusing material moves in both the liquid (vapor) (from hole to hole and over the mean free path, respectively) and structural elements (such as cellular membranes, cytoplasm, and secondary partitions) of the solid by analogy with impurity diffusion in crystals (a hole mechanism, a dissociation-recombination mechanism, and an interchange mechanism [4]). The energy properties of such a body – a mesobody – are special: it combines the properties of a crystal and porous solid, and W_{sol} increases rapidly to the magnitude for crystal bodies or, conversely, decreases rapidly to the magnitude for porous solids. Extraction from mesobodies becomes especially slow, as does sorption of materials by these bodies.

NOTATION

p_{eq}, partial pressure of equilibrium water vapor above a material with a moisture content U; p_{s}, pressure of saturated water vapor at the same temperature; T, temperature; R, gas constant; W, energy of moisture binding; W'_{sol}, W'_{liq}, and $W'_{\mathrm{sol.liq}}$, energy characteristics of a solid, a liquid, and a solid–liquid system, respectively, referred to one molecule of the material; W_{sol}, W_{liq}, $W_{\mathrm{sol.liq}}$, and $W_{\mathrm{sol.sol}}$, energy characteristics of a solid, a liquid, a solid–liquid system, and a solid–solid system, respectively, referred to one mole of the material; $W_{\mathrm{sol}l}$, $W_{\mathrm{liq}l}$, $W_{\mathrm{sol.liq}l}$, and $W_{\mathrm{sol.sol}l}$, same for body of size l; k, Boltzmann constant; D_{liq} and $D_{\mathrm{sol.liq}}$, diffusion coefficients in a free liquid and a solid–liquid system, respectively; δ, elementary travel of a molecule; τ_0, period of molecular vibrations about the equilibrium state; d, effective diameter of the pores; a_{m}, coefficient of mass transfer (moisture transfer) of a porous solid; D_{v}, coefficient of molecular diffusion of a vapor in air; l, geometric parameter (sphere radius, plate half-thickness); N, Avogadro's number.

REFERENCES

1. M. Polanyi, *Zeitschrift für Elektrichemie und angewandte physikalische Chemie*, **25**, No. 7 (1929).
2. P. A. Rebinder, in: *All-Union Scientific-Technical Conference on Intensification of Processes and Upgrading of Materials in Drying in the Basic Industries and Agriculture*, Plenary Meetings (11-15 December 1956) [in Russian], Moscow (1958), pp. 20-33.
3. V. V. Beloborodov, *Inzh.-Fiz. Zh.*, **72**, No. 1, 141-146 (1999).
4. Ya. I. Frenkel', *Kinetic Theory of Liquids* [in Russian], Leningrad (1975).
5. V. V. Beloborodov, *Basic Processes of the Production of Vegetable Oils* [in Russian], Moscow (1966).
6. A. V. Luikov, *Heat and Mass Transfer: Handbook* [in Russian], Moscow (1978).
7. A. G. Neshchadim, *Maslo-Zhir. Promyshl.*, No. 4, 17-19 (1962).
8. A. G. Neshchadim, *Izv. Vyssh. Uchebn. Zaved., Pishch. Tekhnologiya*, No. 4, 53-57 (1963).
9. H. P. Fan, J. C. Morris, and H. Wakeham, *Ind. Eng. Chem.*, **40**, No. 2, 195-199 (1948).
10. L. A. Tarabaricheva, *Study of the Technology of Direct Extraction of Crumbled Sunflower Seeds and the Quality of Products*, Author's Abstract of Candidate's Dissertation in Technical Sciences, Krasnodar (1974).
11. V. V. Klyuchkin, in: *Proceedings of All-Union Scientific-Research Institute of Fats* (Leningrad), Issue 25 (1965), pp. 125-140.
12. J. O. Osborn and D. L. Katz, *Trans. Amer. Inst. Chem. Eng.*, **40**, No. 5, 511-531 (1944).
13. V. V. Beloborodov, *Study of the Mechanism of Extraction of Vegetable Oils*, Candidate's Dissertation in Technical Sciences, Leningrad (1958).
14. A. Kh. Maliev, E. P. Koshevoi, L. A. Koshevatskaya, and V. A. Maslikov, *Izv. Vyssh. Uchebn. Zaved., Pishch. Technologiya*, No. 2, 151-153 (1978).
15. O. Krisher, *Scientific Foundations of Drying Technology* [Russian translation], Moscow (1961).
16. D. K. Berdnikova, *Study of Combined Heat and Mass Transfer in Disperse Media of the Production of Vegetable Oils*, Candidate's Dissertation in Technical Sciences, Krasnodar (1972).
17. V. V. Kafarov, *Principles of Mass Transfer* [in Russian], Moscow (1962).