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Acceleration of chemical processes in aerosol

© *V.B. Fedoseev*

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia
E-mail: vbfedoseev@yandex.ru

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The evolution of the state of aerosol droplets containing a reaction mixture with volatile components is accompanied by a change in the size and composition of the droplets, changes in the concentrations of reagents and the rates of chemical reactions. The methods of formal chemical kinetics and equilibrium thermodynamics describe size effects that lead to a significant acceleration of chemical processes in aerosols. The dependence of the rate of chemical processes on the initial size and composition of droplets, as well as on the composition of the gas phase, is described. The main regularities are modeled on the example of the condensation reaction of glycine with glucose (Maillard reaction).

Keywords: aerosol, size effect, chemical kinetics, spray technology.

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Chemical synthesis in aerosol droplets is one of the trends in development of spray technologies [1–3]. This allows one to perform reactions that require more rigid conditions (catalysts, high temperatures) in macrosystems [4,5]; in addition, states and materials with unique structures [6] or compositions [7,8] may be produced.

The thermodynamic aspect of influence of the aerosol droplet size on the chemical equilibrium was examined in [5]. The kinetic aspect of size effects. which may manifest itself as a variation of rates of chemical processes, is no less important [8,9].

The evolution of aerosol droplets containing a reaction mixture is governed by a combination of interrelated heat- and mass-exchange processes within these droplets and outside of them. Volatile components (solvents, reagents, products, etc.) involved in these processes may alter considerably the volume [10] and chemical composition of droplets and the kinetics of chemical processes [5,8].

Size effects in aerosols rest on the phase equilibrium between condensed and gas phases. Equilibrium concentrations of volatile components are defined by the equality of chemical potentials in coexisting phases, which is represented by the Raoult's (or Henry's) law and Kelvin and Ostwald–Freundlich equations [11]. The dependence of the concentration of volatile components on the gas phase composition is the reason why the droplet radius and the concentration of nonvolatile components change and the chemical equilibrium shifts [3–5,10]. The observed influence of the droplet radius on the chemical equilibrium constant implies that the rates of forward and reverse reactions change accordingly.

Let us illustrate this using the example of a reversible $A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C$ (combination-decomposition) reaction involving nonvolatile components in a volatile solvent. The rates of forward and reverse reactions are

$$v_1 = -k_1 c_A c_B = -k_1 \frac{n_A}{V(r)} \frac{n_B}{V(r)},$$

$$v_2 = k_2 c_C = k_2 \frac{n_C}{V(r)}, \qquad (1)$$

where k_1 and k_2 are the rate constants of forward and reverse reactions, respectively; c_i and n_i are the concentration [mol/l] and the number of moles in a droplet (indices A, B, and C correspond to reagents, while index S denotes the solvent); and r is radius. The concentrations of reagents are related via conservation conditions $n_A + n_B + 2n_C = n_{ini} = \text{const}$ to droplet volume $V(r) = \frac{4}{3}\pi r^3 = \sum n_i V_i$, where V_i are the molar volumes of components, and equilibrium amount of solvent $n_S = x_S(r)\Sigma n_i$ in a droplet with radius r is specified by the Kelvin equation

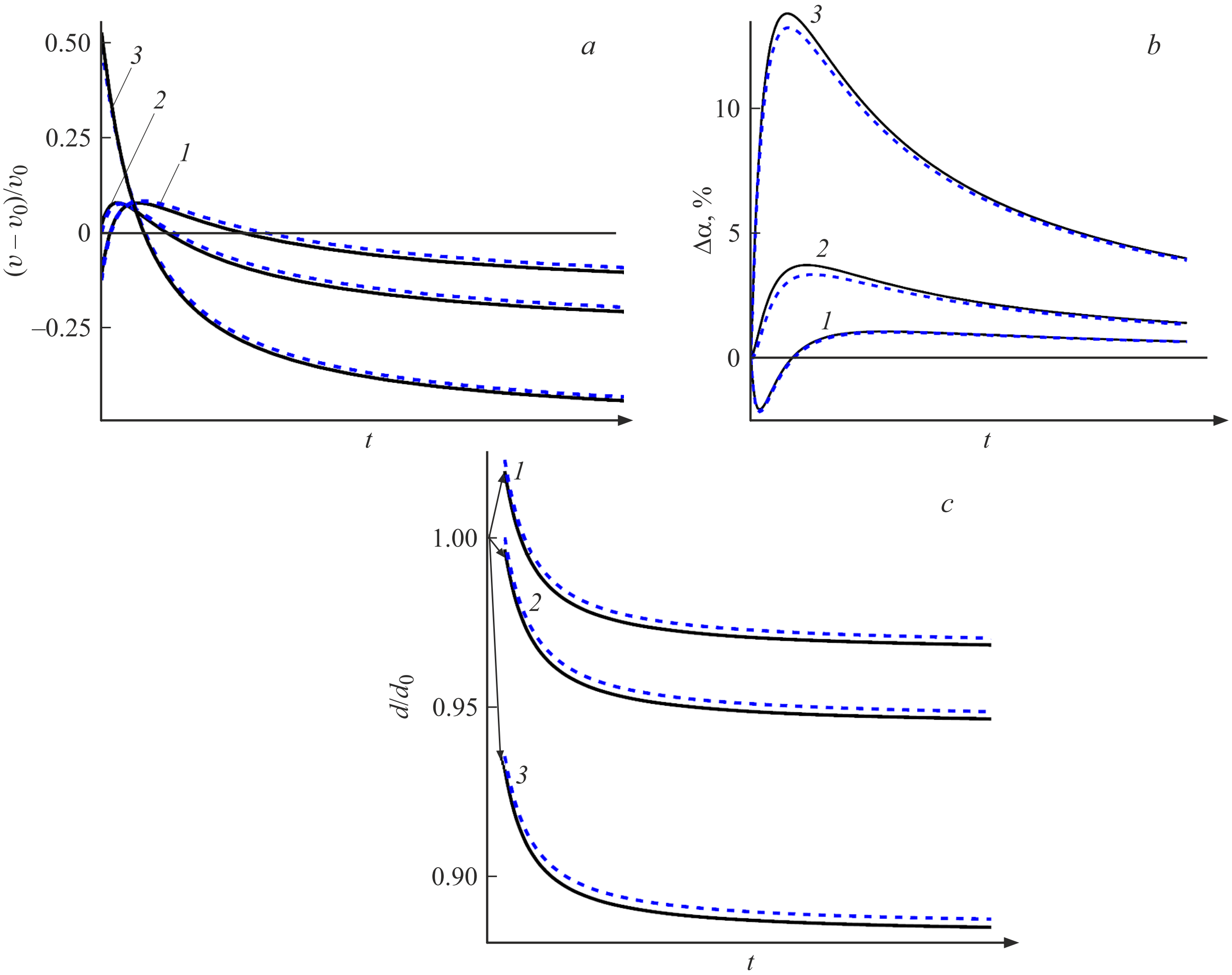
$$x_S(r) = \frac{P_S}{P_{\infty,S}} \exp\left(-\frac{2\sigma V_S}{rRT}\right), \qquad (2)$$

where $P_{\infty,S}$ and P_S are the saturated vapor pressure above a pure solvent and the pressure of solvent in the gas phase, σ is the surface tension, R is the gas constant, and T is temperature.

According to (1), (2), the equilibrium droplet radius is defined unambiguously by the composition of the gas phase and the number of moles of insoluble components: $r = r(n_{ini}, P_S)$. This has several useful corollaries.

1. Coming to equilibrium with a gas medium, droplets of a dilute solution ($x_S > x_S(r)$) grow smaller, evaporating the solvent and raising the concentration of reagents in the process. This translates into an increase in the rates of forward and reverse reactions.

2. Coming to equilibrium with a gas medium, droplets of a concentrated solution ($x_S < x_S(r)$) grow larger, condensing the solvent from the gas phase in the process.



Variation of the reaction rate (v_0 corresponds to a macrosystem) (a), conversion $\Delta\alpha = \alpha - \alpha_0$ (α_0 corresponds to a macrosystem) (b), and the droplet diameter (d_0 is the initial diameter) (c) for aerosols with different initial concentrations: *1* — concentrated ($x_S = 0.1$), *2* — in equilibrium with the gas phase ($x_S = 0.3$), and *3* — dilute ($x_S = 0.6$). Solid and dashed curves correspond to droplets $\sim$ 20–25 nm and $\sim 1\,\mu$m in diameter, respectively.

Decreasing the concentration of reagents reduces the rates of the forward and reverse reactions.

These regularities are applicable to a wide range of reversible and irreversible chemical reactions. Both effects become more pronounced as the droplet radius decreases and factor $\exp\left(\frac{2\sigma V_S}{rRT}\right)$ increases accordingly. This leads not only to a change in reaction rates, but also to a slight shift of chemical equilibrium toward a reduction in the number of moles of nonvolatile reagents (formation of dimers and complex compounds and suppression of dissociation) occurring when the droplet radius decreases.

Processes involving the formation of volatile components (reactions of neutralization, condensation, esterification, polycondensation, etc.) are expected to reveal more complex size effects.

Let us illustrate this using the example of a $A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + S$, condensation reaction with volatile solvent S being one of its products. The rates of forward and reverse reactions are then

$$v_1 = -k_1 c_A c_B = -k_1 \frac{n_A}{V(r)} \frac{n_B}{V(r)},$$

$$v_2 = k_2 c_C c_S = k_2 \frac{n_C}{V(r)} \frac{x_S(r)}{V_m(r)}$$

$$= k_2 \frac{n_C}{V(r)} \frac{1}{V_m(r)} \frac{P_S}{P_{\infty,S}} \exp\left(-\frac{2\sigma V_S}{rRT}\right), \qquad (3)$$

where $V_m(r) = \sum x_i V_i$ is the molar solution volume.

The interaction of amino acids with sugars (Maillard reaction) is an example of a reaction of this kind. Let us assume that A is glucose ($V_A = 115.3\,\mathrm{cm}^3$/mol), B is glycine ($V_B = 46.7\,\mathrm{cm}^3$/mol), C is glycosylamine and the products of its transformation ($V_C = 143.0\,\mathrm{cm}^3$/mol), and S is water ($V_S = 18\,\mathrm{cm}^3$/mol). The reaction of glycine with glucose is characterized formally by a second-order equation [12], proceeds at a very low rate, and is virtually irreversible ($k_2 = 0$).

The results of simulation of kinetics of the reaction between glycine and glucose at $T = 298\,\mathrm{K}$, $P_S = 0.3P_{\infty,S}$ are shown in the figure. Quantity σ assumes a value equal to the surface tension of water and is independent of concentration, since the reagents (glycine and glucose) exert only a weak influence on the surface tension of the solution. The time dimension in $dn_A = dn_B \sim k_1 dt$ is cancelled in integration of Eqs. (3). Choosing the right magnitude of step dt providing a sufficient integration accuracy, one may then set $k_1 = 1$.

The solution concentration comes to equilibrium with the gas phase fairly rapidly through evaporation or condensation of water. This stage is indicated in panel *c* with arrows originating at the state with the initial droplet size ($d/d_0 = 1$). Experimental data [13] suggest that the diameter of solution droplets changes rather rapidly (from 100 to $10\,\mu$m and back in a fraction of a second). Rapid evaporation or condensation governs the initial reaction rates in a droplet. Even if $v < v_0$ at the initial moment, the rate of condensation reaction in droplets soon becomes higher than the corresponding rate in a macrosystem (curve *1* in panel *a* of the figure). The conversion ($\alpha = 2n_C/n_{ini}$) and dynamics of evaporation are governed solely by the current composition of reagents in a droplet. In the general case, dilution of the initial solution of reagents contributes to a considerable increase in the process rate (as in (1)). Since the solvent concentration depends on radius (2), the reaction rate in nanometer droplets is higher than the one in micrometer-sized droplets (see the figure). The smaller the droplet diameter is, the faster and more efficient is the process of equilibration with the gas phase and maintenance of this equilibrium via interphase heat and mass exchange.

The figure illustrates the key difference in kinetics between combination (1) and condensation (3) reactions. Although the reaction rate decreases at the initial moment due to absorption of a solvent from the gas phase, the removal of a volatile product in reaction (3) contributes to an increase in the current conversion and speeds up the reaction in aerosol (compared to the same reaction in a macrosystem) even in concentrated solutions (curve *1* in panels *a* and *b* of the figure).

Size effects are most pronounced in reactions associated with a considerable reduction in the number of moles of nonvolatile components (polycondensation, polymerization, precipitation of a product to the solid phase). Experimental data [14] provide convincing proof that the rate of polycondensation of lactic acid depends heavily on the droplet size. In fact, it is comparable under normal conditions to the rate of a catalytic process at a high temperature in a macrosystem.

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Conflict of interest

The author declares that he has no conflict of interest.

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