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Abstract

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SURFACE EFFECT OF A CHEMICAL PROCESS

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It is known that the presence of a gradient of one property induces, in certain cases, a gradient of another (thermoelectric phenomena, thermal diffusion, electrodiffusion potential, etc.). It is of interest to consider under what conditions a gradient of chemical potential (a chemical reaction) can directly lead to a gradient of temperature, electric potential, and so on. This article discusses the conditions for the direct conversion of the free energy of a chemical process into surface energy. A chemical process that is taking place can, under certain conditions, cause an increase in the phase-boundary surface, i.e., can affect the magnitude of the surface tension.

The formal relations for describing the phenomenon are provided by the thermodynamics of irreversible processes. Let there be no chemical equilibrium in a system consisting of two phases. For simplicity we shall confine ourselves to considering the transformation of one component. Then the flux of this component from one state to another, I_1, depends on the corresponding generalized force X_1, equal to the potential difference $\Delta\mu$. In addition, the surface in the system may change. The corresponding flux I_2 will be determined by the generalized force X_2, which can be found on the basis of the known relation $T\theta_2 = I_2 X_2$. The rate of increase of entropy θ_2 due to an increase of the surface A is equal to

$$\frac{dA}{d\tau}\left(-\frac{\Delta H_\sigma}{T} + \Delta S_\sigma\right),$$

where $\Delta H_\sigma = \Delta\sigma - T\frac{\partial\Delta\sigma}{\partial T}$ is the change in heat content when the surface is changed by a unit area, $\Delta S_\sigma = -\frac{\partial\Delta\sigma}{\partial T}$. The flux $I_2 = \frac{dA}{d\tau}$. Therefore,

$$X_2 = -\Delta\sigma. \tag{1}$$

Here dA is the change in that part of the interfacial surface on which the flux I_1 takes place at the expense of the remaining surface; $\Delta\sigma$ is the change in surface tension caused by the flux I_1. The generalized Onsager equations for the case under consideration are written as follows:

$$I_1 = L_{11}X_1 + L_{12}X_2; \quad I_2 = L_{21}X_1 + L_{22}X_2. \tag{2}$$

Let the value $\Delta\mu$ be specified and maintained. Then in the steady state $I_2 = 0$, and according to (2)

$$\frac{X_2}{X_1} = -\frac{L_{21}}{L_{22}}. \tag{3}$$

If, at $\Delta\mu = 0$, the surface area is increased by one unit, then, generally speaking, I_1 moles of the component will be transferred from one state to another. According to (2) this quantity is determined as follows:

$$M = \left(\frac{I_1}{I_2}\right)_{\Delta\mu=0} = \frac{L_{12}}{L_{22}}. \tag{4}$$

Since $L_{12} = L_{21}$, in accordance with (3) and (4) we have:

$$\Delta\sigma = M \cdot \Delta\mu. \tag{5}$$

By analogy with heat transfer, M may be called the surface-transfer number of the component. The effect of a chemical process ($\Delta\mu$) on a change in surface tension ($\Delta\sigma$) is possible only if the surface-transfer number is nonzero. This can be realized, for example, in the following case. Let the intermediate

compound (or series of states) in the chemical process under consideration is more surface-active than the initial and final states. The presence of a capillary-active intermediate compound is a necessary, but not sufficient, condition. It must be required that the concentration of this compound not be too small. Since, in a stationary flow, this concentration depends on the ratio of the rate constants of its formation and decomposition, corresponding requirements arise for the kinetic characteristics. In particular, if the process consists in the transfer of a component from one phase to another, it is necessary to require a high rate of sorption and a low rate of desorption of the intermediate compound.

An increase in the interfacial surface under conditions of chemical equilibrium should lead to an increase in the number of moles of the surface-active intermediate compound, which, generally speaking, is associated with the disappearance of molecules in the two states under consideration in proportions not corresponding to equilibrium concentrations and, consequently, with the subsequent transition of one state into another. The requirements on the kinetic characteristics indicated above ensure such a transition. In accordance with the more general formulation of the problem stated at the beginning of the article, one may assert that the introduction into an equilibrium system of some new state of the molecules will lead to transfer of the component. From what has been said it follows, in particular, that a catalyst must have a reduced value of the surface tension during the catalytic process.

The effect of the capillary activity of a chemical process can be illustrated by four groups of experiments. A number of investigators ($^{1-3}$) observed that, in the presence of a chemical process of interphase transfer of components in a metal—slag system, a change occurs in the shape of a metal droplet situated in the slag. The authors associated this phenomenon, in more or less explicit form, with the fact of chemical interphase transfer.

Another qualitative illustration of the decrease in σ as a result of a parallel chemical process is the previously observed autoemulsification initiated by a chemical reaction (^{4}).

For a quantitative description of the phenomenon under discussion, we undertook two groups of measurements of the surface tension under conditions of a parallel chemical process, using the method of maximum pressure in a bubble and the drop-counting method. In the first of these methods, two capillaries were immersed in the solution under study at a small distance from one another. Nitrogen was blown through one of them, and through the other—a mixture of nitrogen with the chemical reagent. Figure 1 gives the results of measuring σ for a 20 wt.% HCl solution. Time is plotted on the abscissa axis. The ordinate axis gives the value of σ. The first curve conveys the results obtained on the capillary through which nitrogen was supplied. The second—the mixture of nitrogen with 75% ammonia. As additional measurements showed, point b corresponds to the precipitation of salt from the solution, point c to the end of the neutralization process. Figure 2 gives an analogous curve when gaseous HCl was blown through a 20% solution of NH_3. A detailed interpretation of these curves is not simple, since, despite vigorous stirring, local differences in concentration at the ends of both capillaries are possible. We note, however, two striking characteristic features that are in accord with the effect under consideration: at the initial moments of time (point a), the value of σ in the presence of the chemical process always proves to be lower than that measured by the capillary through which nitrogen was blown. In the case described by the curve in Fig. 2, this decrease cannot be explained by a local change in concentration. The second essential feature of the process is the presence of a plateau. The surface tension remains practically unchanged over a wide interval of concentration change. At the same time, the value of σ at the plateau level increases substantially with decreasing capillary diameter. The phenomenon of independence of σ from concentration is manifested most strongly in the following experiment. If a saturated NH_4Cl solution contains some concentration of one

of the reactants, while the second is in the gas mixture, the measured σ proves to be substantially lower than that measured when nitrogen is used; it coincides with the value of σ on the plateau (Figs. 1 and 2) and likewise does not depend on the concentration of the reagent in solution. In this case, very small additions of reagent to a saturated NH_4Cl solution are sufficient to reduce the value of σ from a quantity of the order of 80 erg/cm^2 to 74.6 (capillary diameter

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

1.75 mm). The observed effect of the independence of σ from concentration corresponds to the phenomenon under consideration, if it is assumed that the capillary-active intermediate compound is formed mainly at the expense of the component located in the gas phase. The dependence of the plateau value of σ on the capillary diameter is explained by the fact that the capillaries create an additional resistance to the flow. The magnitude of the jump in chemical potential $\Delta\mu$, which actually exists at the interface, depends on the capillary diameter.

Fig. 1. Change in surface tension (σ) in the course of the chemical reaction NH_3 (gas) +HCl (solution) $\rightarrow$ NH_4Cl.
1 $-\sigma$ of the solution at the boundary with nitrogen, **2** $-\sigma$ of the solution at the boundary with a mixture of nitrogen and 75% ammonia, capillary diameter 2.05 mm, **3** –see 2, capillary diameter 1.75 mm, **4** –see 2, capillary diameter 0.90 mm, **5** $-\sigma$ of saturated NH_4Cl solution at the boundary with nitrogen, **6** $-\sigma$ of H_2O at the boundary with nitrogen, **7** $-\sigma$ of 20% NH_4Cl solution at the boundary with nitrogen.

Fig. 2. Change in surface tension (σ) in the course of the chemical reaction HCl (gas) +NH_3 (solution) $\rightarrow$ NH_4Cl.
1, 5, 6 –as in Fig. 1, **2** $-\sigma$, measured at the boundary of the solution with gaseous HCl, capillary diameter 1.75 mm, **3** –see 2, capillary diameter 2.05 mm, **4** $-\sigma$ of a 20% aqueous NH_3 solution at the boundary with nitrogen.

In order to prove that the observed effects cannot be explained by peculiarities of the method used, we measured σ in the same system by the drop-counting method. Drops of the solution under study, containing one of the reactants, fell into a vessel through which a gas mixture containing the second reagent was passed. The results obtained by the stalagmometric method are in complete agreement with the measurements made by the maximum bubble-pressure method. Thus, for example, the value of σ of a saturated NH_4Cl solution containing HCl, in the case where the gas phase contains NH_3, is equal to 70.4 erg/cm^2 and does not depend on the concentration of hydrochloric acid, whereas σ, measured in the absence of ammonia in the gas phase, varies with the concentration of HCl in solution in the interval from 81.7 (without HCl) to 79.6 erg/cm^2 (2% HCl).

The reduction effect of σ under discussion differs from dynamic surface tension in that it persists for as long as desired, provided the magnitude of $\Delta\mu$ is maintained.

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REFERENCES

1. R. Kozakevitch, G. Urbain, M. Sage, *Rev. Metallurgie*, **52**, No. 2, 161 (1955).
2. S. I. Popel' , O. A. Esin et al., *DAN*, **112**, No. 1, 104 (1957).
3. A. A. Leont' eva, *Koll. zhurn.*, **11**, issue 3, 176 (1949).
4. W. D. Harkins, H. Zollman, *J. Am. Chem. Soc.*, **48**, No. 1, 69 (1926).

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