The Ostwald Step Rule

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The empirical observation that crystallization from a solution occurs in steps in such a way that often thermodynamically unstable phases occur first, followed by the thermodynamically stable step (Ostwald's step rule), still has no theoretical foundation. Here it is demonstrated that Ostwald's step rule can be related to irreversible thermodynamics. It is shown that Ostwald's step rule minimizes entropy production.

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Introduction

If a reaction can result in several products, it is not the stablest state with the least amount of free energy that is initially obtained, but the least stable one, lying nearest to the original state in free energy. This statement constitutes Ostwald's step rule on the law of successive reactions.[1] Elucidation of this rule has become relevant to our research in view of similar observations made during zeolite synthesis.[2]

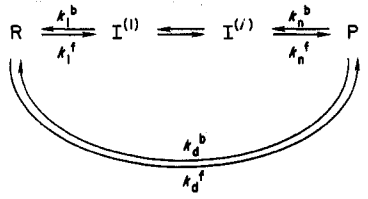
The present Letter aims to elucidate Ostwald's empirical rule, using results of the theory of nonequilibrium thermodynamics.[3-5]

According to the second law of equilibrium thermodynamics, entropy increases or remains constant when a transformation occurs. Here we will show that, if some conditions are satisfied, entropy production is decreased in transformations following the law of successive transformations.

Nonequilibrium thermodynamics teaches that entropy production is minimum in the stationary state.[3,6] So, as a consequence of the step rule the dynamics of the system approaches stationary-state behavior and each transformation occurs as close to reversibility as possible.

Derivation

The reaction scheme considered is



We compare the entropy production for the transformation from R to P via intermediates $I^{(i)}$ and for direct transformation from R to P.

Defining the equilibrium constants K_d and K_i as

$$K_d = \frac{k_d^b}{k_d^f} \qquad K_i = \frac{k_i^b}{k_i^f} \tag{1}$$

one finds

$$K_d = \prod_i K_i \tag{2}$$

The entropy production σ due to a chemical reaction is[4]

$$\sigma = -\sum_{j=1}^{r} J_j \frac{A_j}{T} \tag{3}$$

where r is the number of reactions taking place between the components of the system. The total rates of formation of component j, J_j, are defined by

$$\rho \frac{dc_i}{dt} = \sum_{j=1}^{r} r_{ij} J_j \tag{4}$$

ρ being the mass density, and the affinities A_i by

$$A_i = \sum_{j=1}^{n} r_{ij} \mu_j \tag{5}$$

r_{ij} divided by the molecular mass m_i is proportional to the stoichiometric coefficient of species i in reaction j. Close to equilibrium the chemical potential μ_i is given by

$$\mu_i = \eta_i(T) + RT \ln c_i \tag{6}$$

For reactions following first-order kinetics one finds

$$J_i = k_1^f c_{i-1} \left(1 - \frac{k_i^b}{k_i^f} \frac{c_i}{c_{i-1}} \right) = k_i^f c_{i-1} (1 - e^{A_d/RT}) \tag{7}$$

In the general case one finds[7]

$$J_i = w_i^f - w_j^f = w_i^f (1 - e^{A_i/RT}) \tag{8}$$

with w_i^f and w_i^b being the forward and backward rates of formation of product i.

Close to equilibrium the entropy production reduces to

$$\sigma = \frac{1}{RT^2} \sum_{i=1}^{n} w_i^f A_i^2 \tag{9}$$

If no intermediates $I^{(i)}$ are formed, but direct transformation from R and P occurs, the expression for the entropy production σ_d becomes

$$\sigma_d = -J_d \frac{A_d}{T} \tag{10}$$

with

$$J_d = w_d^f (1 - e^{A_d/RT}) \tag{11}$$

Using (2) one derives

$$A_d = RT \ln \frac{k_d^b}{k_d^f} \frac{c_p}{c_R} \tag{12a}$$

$$= RT \ln \frac{c_p}{c_R} + RT \sum_i \ln K_i \tag{12b}$$

$$= \sum_i A_i$$

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So close to equilibrium one derives

$$\sigma_d = \frac{w_d^f}{RT^2}(\sum_{i=1}^{n} A_i)^2 \quad (13)$$

So, if

$$w_i \approx w_d \quad \text{and} \quad n > 1 \quad (14a)$$

$$\sigma < \sigma_d \quad (14b)$$

Expression 14 is the desired result, showing that the entropy production of the stepped process is lowest as long as conditions 14a are satisfied.

Relation 9 can be reformulated in the case the system is assumed to be stationary, since all J_i are then equal

$$J = J_i = -w_i^f \frac{A_i}{RT} = -w \frac{\sum_i A_i}{RT} \quad (15)$$

with[5]

$$\frac{1}{w} = \sum_i \frac{1}{w_i} \quad (16)$$

Expression 9 now reduces to

$$\sigma = \frac{w}{RT^2}(\sum_i A_i)^2 \quad (17)$$

So

$$\frac{\sigma_d}{\sigma} = \frac{w_d^f}{w} = \sum_i \frac{w_d^f}{w_i^f} \quad (18)$$

If (14a) is satisfied, this quotient $\approx n$, with $n - 1$ being the number of intermediates formed.

Conclusion

The result, relation 18, is very revealing, since it shows that entropy increase minimization is not due to a lower rate of the direct process but is caused by the multiple nature of the indirect process.

Determination of the Number of d-Electron States in Transition-Metal Compounds

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The d-electron population of first-row transition-metal elements in several simple compounds can be determined with high spatial resolution on minute samples, using electron-energy-loss spectroscopy carried out with an electron microscope.

X-ray absorption edge spectra can be used to yield quantitatively reliable values for the number of unoccupied d-electron states in a metal. In a recent example,[1] a correlation was established between the area under each of the L_2 and L_3 X-ray absorption edges and d-band vacancies in platinum-containing materials which exhibit so-called white lines (that arise from transitions from the $2p_{3/2}$ and $2p_{1/2}$ levels to the unoccupied 3d states). The intensities of Auger-electron transitions are also governed by the number of valence electrons present in the element under consideration. And in the case of first-row transition metals and their oxides for example, the following relationships[2,3] between Auger intensity ratios and the number of valence electrons, N, are obeyed:

$$L_{23}M_{23}M_{45}/L_{23}M_{23}M_{23} \propto N$$

$$L_{23}M_{45}M_{45}/L_{23}M_{23}M_{45} \propto N - 1$$

Useful as these facts are, they do imply that advantage can be taken of the quantitative relationships only in analyses which are nonspatially resolved, at least until such time as "dispersive" EXAFS becomes available. All too often, however, the need arises to pinpoint the oxidation state of a transition element when multicomponent or heterogeneous systems are under consideration, as is almost invariably the case in the study of heterogeneous catalysts. Under such circumstances, a technique which can focus on ultramicroscopic quantities and still yield the number of d-electron states would be an advantage.

We have explored the use of electron energy loss spectroscopy (EELS) carried out in an electron microscope[4-6] for such purposes. We summarize here some of the salient results that demonstrate the utility of this technique, along with its added power over its X-ray absorption-edge analogue in that it can conveniently cope with additional analytical problems involving light elements (from Li, $Z = 3$ upward). At present, X-ray absorption edge measurements with synchrotron radiation are unfortunately limited[7] to elements beyond Ca, $Z = 20$.

Using a conventional electron microscope fitted with an electron spectrometer (Gatan Model 607 magnetic prism type[8]), we have studied the metal L edges as well as the oxygen K edges in a number of transition-metal oxides. In particular, we find that the intensities of the L_2 and L_3 white lines (Figure 1) decrease progressively as the number of unoccupied d-electron states decreases. Thus, the L_3 intensity is zero in copper metal and in Cu_2O (both with d^{10} configuration) and has a finite value in CuO; whereas in the series of manganese oxides, the L_3 intensity is least in $MnO(d^5)$ and highest in $KMnO_4(d^0)$. The full width at half-maximum intensity (fwhm) of the L_3 white line also shows a marked decrease (from a value of ca. 6 eV in $KMnO_4$ to ca. 4 eV in MnO). Plots of the intensity or of the fwhm against the d orbital occupancy (Figure 1) can be utilized to estimate the number of d-electron states in an unknown. We have further found that the L_3/L_2 intensity ratio is not constant in a series of oxides of a given transition metal and that it varies widely from the value

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