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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.

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.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.3,4

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.3,5 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

\[ \text{R} \xrightarrow{k_0} \text{I}^0(1) \xrightarrow{k_1} \text{I}^1 \xrightarrow{k_2} \text{P} \]

We compare the entropy production for the transformation from R to P via intermediates \( \text{I}^0 \) and for direct transformation from R to P.

Defining the equilibrium constants \( K_d \) and \( K_i \) as

\[ K_d = \frac{k_0^b}{k_1^b}, \quad K_i = \frac{k_2^b}{k_2^f} \]

one finds

\[ K_d = \prod_i K_i \]  

The entropy production \( \sigma \) due to a chemical reaction is

\[ \sigma = \frac{1}{T} \sum_{i=1}^{n} A_i \frac{d}{dt} \ln K_i \]

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

\[ \dot{c}_j = k_i \frac{d}{dt} c_j \]

\[ \rho \] being the mass density, and the affinities \( A_i \) by

\[ A_i = \sum_{j=1}^{n} r_j \mu_j \]

with \( \mu_j \) divided by the molecular mass \( m_j \) is proportional to the stoichiometric coefficient of species \( j \) in reaction \( i \). Close to equilibrium the chemical potential \( \mu_i \) is given by

\[ \mu_i = \mu_i(T) + RT \ln c_i \]

For reactions following first-order kinetics one finds

\[ J_i = k_i c_i \left( 1 - \frac{c_i^b}{k_i^b c_i^0} \right) = k_i c_i \left( 1 - e^{A_i/RT} \right) \]

In the general case one finds

\[ J_i = \dot{w}_i + \dot{w}_i^b = \dot{w}_i (1 - e^{A_i/RT}) \]

with \( \dot{w}_i \) and \( \dot{w}_i^b \) being the forward and backward rates of formation of product \( i \). Close to equilibrium the entropy production reduces to

\[ \sigma = \frac{1}{RT} \sum_{i=1}^{n} \dot{w}_i A_i \]

If no intermediates \( I^0 \) are formed, but direct transformation from R and P occurs, the expression for the entropy production \( \sigma_d \) becomes

\[ \sigma_d = -J_d \frac{A_d}{T} \]

with

\[ J_d = \dot{w}_d (1 - e^{A_d/RT}) \]

Using (2) one derives

\[ A_d = RT \ln \frac{k_0^b c_0}{k_2^b c_R} \]

where

\[ R \]

are

\[ \sum_i A_i \]

So close to equilibrium one derives

\[ \sigma_d = \frac{w_d f}{RT^2} \left( \sum A_i \right)^2 \quad (13) \]

So, if

\[ \sigma = \frac{w}{RT^2} \left( \sum A_i \right)^2 \quad (16) \]

Expression 9 now reduces to

\[ \sigma = \frac{w}{RT^2} \left( \sum A_i \right)^2 \quad (17) \]

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 L2 and L3 X-ray absorption edges and d-band vacancies in platinum-containing materials which exhibit so-called white lines (that arise from transitions from the 2p3d and 2p3p 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:

\[ \frac{L_{23}M_{23}M_{45}}{L_{23}M_{23}M_{23}} \propto N \]
\[ \frac{L_{23}M_{23}M_{45}}{L_{23}M_{23}M_{23}} \propto N - 1 \]

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 a electron microscope4 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 limited2 to elements beyond Ca, Z = 20.

Using a conventional electron microscope fitted with an electron spectrometer (Gatan Model 607 magnetic prism type6), 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 L2 and L3 white lines (Figure 1) decrease progressively as the number of unoccupied d-electron states decreases. Thus, the L3 intensity is zero in copper metal and in Cu2O (both with d10 configuration) and has a finite value in CuO; whereas in the series of manganese oxides, the L3 intensity is least in MnO(d9) and highest in KMnO4(d5). The full width at half-maximum intensity (fwhm) of the L3 white line also shows a marked decrease (from a value of ca. 6 eV in KMnO4 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 L1/L2 intensity ratio is not constant in a series of oxides of a given transition metal and that it varies widely from the value with additional analytical problems involving light elements (from Li, Z = 3 upward).

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