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Ionic Exchange Equations Derived From Statistical Thermodynamics

C. Krishnamoorthy, L. E. Davis, and R. Overstreet

Division of Soils,
University of California, Davis

Ionic exchange systems at equilibrium consist of two phases: an aqueous phase, which may be a filtrate or a centrifugate, and an adsorbent phase, which is the solid exchanger. Equilibrium states may be defined in terms of equations which represent the distribution of ionic species between the two phases. Many of the theoretical expressions which appear in the literature have the form of mass action equations. We may postulate that such expressions are well defined thermodynamically when the terms employed consist of ratios of appropriate powers of so-called ionic activities.

We cannot directly measure the activity values in the adsorbent phase. Special working hypotheses can be tested. The usual test employed is invariance of the equilibrium "constant" when concentrations are varied.

Kerr (*3*) and others have assumed tacitly or specifically that the ionic activities are equal to the concentrations of the exchanging ions in the adsorbent phase. Vanselow (*4*) has shown that this assumption does not generally lead to invariant values of the exchange constant. This is particularly true for unidivalent exchanges when the amount of exchanger is varied. Vanselow proposed the hypothesis that ionic activities of ions in the adsorbed state are equal to mol fractions. In many cases more consistent results were obtained when this hypothesis was employed.

Recently Davis has adopted a method first presented by Fowler and Guggenheim (*1*) and applied by them to equilibrium adsorptions of mixed gases on surfaces. Each gas molecule is assumed to be adsorbed onto one site on the surface. Guggenheim (*2*) has extended the discussion to include cases in which certain molecules occupy more than one site. The activities of the adsorbed species are related to the number of mols by equations which can be derived from a relatively simple statistical mechanics.

This procedure can be applied to ionic exchange "adsorption" states with a slight modification of the basic assumptions utilized by Fowler and Guggenheim. Each adsorbed ion is present in a quasi-ideal monolayer. The nature of the forces or bonds is irrelevant except that the partition function must be independent of the ionic distribution. This is probably true for completely dissociated ions, but not, apparently, for hydrogen and perhaps other ions. The ions interact electrostatically. However, unless the interaction is specific, it will not vary with the relative amounts of the ionic species, since the total number of adsorbed elemental charges per unit area of monolayer is invariant. (There are no unoccupied sites.) This condition is equivalent to the assumption utilized by Guggenheim that the energy of mixing is zero.

The derivation will not be presented here, but the final expression is shown as equation (1). The authors have assumed herein that each site on the adsorbing surface has four nearest neighboring sites. In equations (1) and (2), terms in brackets represent numbers of mols of replaceable ions in the adsorbent phase, Z. Terms in parentheses represent "ionic activities" in the aqueous phase. For a system containing in the aqueous and adsorbent phases the ionic species A, B, C, D, . . . of valencies r_1, r_2, r_3, r_4, . . . r_n, the equilibrium for the exchange reaction of any pair, say A and B, is given by the expression:

$$k_{(A,B)} = \frac{[A]^{r_2}}{[B]^{r_1}} \cdot [q_1 A + q_2 B + q_3 C + \ldots\ldots]^{r_1 - r_2} \cdot \frac{(B)^{r_1}}{(A)^{r_2}}, \qquad (1)$$

where $q_n = \frac{r_n + 1}{2}$ for the assumption that each site on the absorbing surface has four neighboring sites.

For a system containing La, Cs, and H, equation (1) reduces to

$$k_{(La,Cs)} = \frac{[La]}{[Cs]^3} \cdot [Cs + H + 2La]^2 \cdot \frac{(Cs)^3}{(La)}. \qquad (2)$$

The presence of variable amounts of H in systems with varied concentrations of the three ionic species may invalidate to some extent the assumption that interaction is invariant. However, when H is not one of the reacting pair A and B, the effect is indirect and possibly not important to a first approximation.

Equation (2) has been tested experimentally with clays and synthetic resins by Krishnamoorthy and Overstreet. The results for the synthetic resin IR 100 are presented below:

	[La]	[Cs]	[H]	(La)	(Cs)	$k_{(La,\,Cs)}$ (Equation 2)
1	.174	.692	.520	$.15 \times 10^{-3}$	.324	345
2	.345	.373	.330	2.33×10^{-3}	.389	385
3	.407	.110	.370	.114	.398	385
4	.433	.090	.300	.258	.418	379
5	.094	.036	.100	.073	.472	355
6	.167	.182	.230	1.5×10^{-3}	.326	357
				Avg.		367 ± 14

All quantities in the table are expressed as millimols/100 cc, and the constant $k_{(La,Cs)}$ has been corrected for activity coefficients of ions in the aqueous phase. An extension of Guggenheim's theory is being applied to a variety of systems. The results will be published elsewhere.

References

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Cleavage Patterns Disclose "Toughness" of Metals[1]

C. A. ZAPFFE, C. O. WORDEN, JR., and
F. K. LANDGRAF, JR.

6410 Murray Hill Road, Baltimore, Maryland

A recent communication in this journal (*1*) called attention to the microscope technique referred to as "fractography," particularly with respect to its usefulness in disclosing subtle structural deformities within crystals relating to their history and mechanism of growth.

Now it is found that the cleavage patterns studied by fractography similarly contain marked features directly related to the "toughness" of the crystal. In the case of engineering materials, particularly metals, "toughness" is a most important property, and one which has escaped satisfactory measurement to date. That is, values for tensile strength were long ago found to be inadequate as a measure of structural stability if the material was stressed nonaxially, such as by bending or by lateral impact, and auxiliary values for ductility, hardness, and impact resistance were subsequently added to specifications. Experience during the recent war, however, emphasized the fact that the true measure for "toughness" still does not stand among any of these values. A phenomenon in point is that in which apparently identical steels used for ship-plate served in a satisfactory manner in one case, but in the other failed suddenly, and often disastrously, in a brittle fashion, indicating some radically inferior property of the metal not yet recognized. Among these experiences are some 4,000 reported failures on welded ships, some 40 of the vessels having broken completely in two.

Recently it has been determined by metallurgists working on the problem, principally under the sponsorship of the U. S. Navy, that this difference in "toughness" can be demonstrated in the laboratory by conducting certain standard tests over a range of temperature—for example, fracturing by impact a series of notched specimens at progressively lowered temperatures. The energy absorbed by the specimen commonly has an acceptably large value when fractured in the high range of ordinary temperatures; but, as the temperature lowers toward and into the freezing range, certain steels rapidly lose their resistance to fracture. The narrow temperature range in which this defection appears is currently referred to as the "transition temperature"; and the phenomenon shows simultaneously as a loss in resistance to propagation of fracture, a failure of the crystal's slip elements to provide the malleability which characterizes good metal, and a change in the macro-appearance of the fracture surface from ductile-fibrous to brittle cleavage.

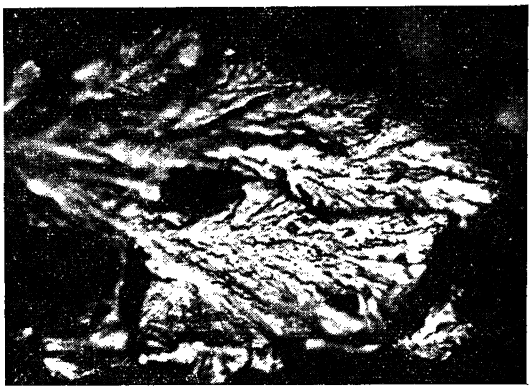

FIG. 1. *Pattern of "toughness."* A cast steel containing 7.70% chromium and 0.10% carbon, air-cooled from 875° C to produce martensite (x 2,000).

In this laboratory the cleavage facets of individual grains within structural steels have been examined at high magnification; and the discovery of a cleavage pattern having marked relationships with "toughness," as determined both by mechanical testing and by actual service, provides the basis for this communication.

The cleavage facet shown in Fig. 1 is in a martensitic structure, which is known to be "tough." The pattern accordingly discloses a rough surface visibly indicating an almost continuous interruption of cleavage traverse. Crystallographic markings are absent. The grain size is also small, imposing an additional hindrance by requiring frequent change in the general plane of traverse as the separation proceeds from grain to grain. In this steel, cleavage is therefore resisted both transgranularly and intergranularly.

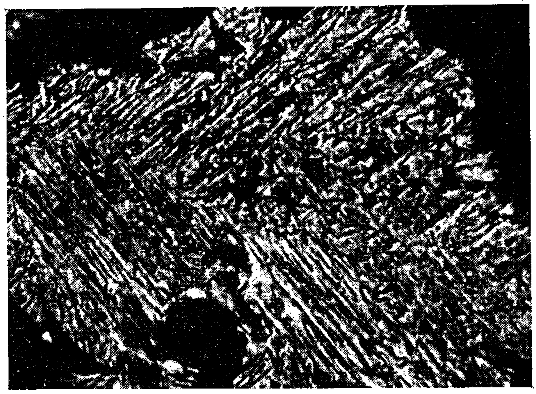

FIG. 2. *Pattern of weakness.* Type 446 stainless steel, containing 26% chromium and 0.15% carbon, water-quenched from 850° C and embrittled by heating for 200 hrs at 475° C (x 850).

The fractograph of another chromium-containing steel (Fig. 2) shows a markedly different pattern. This is a

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[1] From research conducted in the laboratory of the senior author under contract with the Office of Naval Research.