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ChE letter to the editor

LANGMUIR'S ISOTHERM:

Kinetics or Thermodynamics?

Dear Sir:

The Langmuir isotherm for adsorption equilibrium of m solutes is of the form

$$q_j = \frac{a_j c_j}{1 + \sum_{i=1}^m b_i c_i} \quad (j=1, \dots, m) \quad (1)$$

where the q_i and c_i are the concentrations of the solutes i on the adsorbent and in the fluid phase, respectively, and the a_i and b_i are constant coefficients. Langmuir⁽¹⁾ derived his equation in 1916 with a kinetic argument: that the rates of adsorption and desorption must be equal at equilibrium.

To this day almost every textbook follows his reasoning, even though it does not stand up too well to close scrutiny. It postulates the adsorption rate to be proportional to the concentration of the solute in the fluid phase and the unoccupied surface area; and the desorption rate to the amount adsorbed.

While this is plausible, there is no proof. Also, in reality, adsorption and desorption rates often are controlled by mass transfer and so may obey different laws. The derivation should therefore retreat to declaring its rates as only those of attachment to and detachment from the surface,⁽²⁾ and even then the rate law may differ if attachment and detachment were to involve more than a single step.

More seriously, where Langmuir's equation is not obeyed, do we really believe the deviation is caused by a kinetic anomaly? Lastly, have we not warned our students on other occasions that intermingling kinetic and equilibrium arguments is fraught with pitfalls?

Although its original derivation is shaky, the Langmuir isotherm has proved to be more successful than any other of comparable simplicity. So why not show our students a derivation that is more convincing and free of merely

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plausible assumptions?

The isotherm describes adsorption *equilibrium*, and the finest tool we have for equilibria is thermodynamics. We used thermodynamics to derive the mass-action law. To recapitulate: The Gibbs free energy of a (closed) system is a function only of temperature, pressure, and conversion and is at its minimum at equilibrium; with m participants, stoichiometric coefficients ν_i , and at constant temperature and pressure

$$dG = \sum_{i=1}^m \frac{\partial G}{\partial n_i} dn_i = 0 \quad (2)$$

at equilibrium, where n_i is the number of moles of species i . Introducing the chemical potential μ_i and its concentration dependence

$$\frac{\partial G_i}{\partial n_i} \equiv \mu_i = \mu_i^\circ + RT \ln c_i$$

provided the system is ideal (activities equal concentrations). The reaction stoichiometry requires

$$dn_i \propto \nu_i$$

so that

$$\sum_{i=1}^m \nu_i \mu_i = \sum_{i=1}^m \nu_i \mu_i^\circ + RT \sum_{i=1}^m (\nu_i \ln c_i) = 0$$

at equilibrium. Since the term involving the standard potential, μ_i° , is constant

$$\prod_{i=1}^m c_i^{\nu_i} \equiv K = \text{const.} \quad (3)$$

at equilibrium. This is the mass-action law, with K as the equilibrium constant.

Nowhere in this derivation was it necessary to assume chemical bonds to be formed or broken, or even to identify the participants as molecules or chemical species. The derivation covers any kind of process in which something is changed into something thermodynamically distinguishable. Its result can therefore be applied to adsorption as well, and it yields the Langmuir isotherm.

An easy way of showing the long-known mathematical equivalence of the mass-action law and Langmuir isotherm is as follows. For the reversible "reaction" of a solute molecule j with free adsorbent surface to form occupied surface, the mass-action law gives

$$\frac{\theta_j}{\theta_{\text{free}} c_j} = K_j = \text{const.} \quad (4)$$

where the free and occupied surface are expressed as fractions θ of total surface. Also

$$\theta_{\text{free}} = 1 - \sum_{i=1}^m \theta_i \quad (5)$$

From Eq. (4)

$$\frac{\theta_i}{\theta_j} = \frac{K_i c_i}{K_j c_j} \quad (6)$$

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related with separation steps and are generally used when a precipitate or an easily separable gas is formed. When a change of crystal structure is required, the corresponding reaction will be the latest step in the process.

Following the scheme given for organic processes, the next step in process synthesis is to decide the species allocation, *i.e.*, the route of each species through the process. Thus, quantity and reactivity of impurities permit one to decide if they are processed or not. If there are ions in the solution, every valuable product or by-product and every group of species with waste destination and similar solubility will constitute an outlet. Recirculation of the mother liquor, with a purge to avoid the build-up of impurities, can be convenient.

The general structure of the separation system depends upon the phases leaving the reactor. In every case, first separation is a phase split, and after that the stream of each phase is driven to the corresponding separation system (solid, liquid, or gas). From each separation system, streams of different phases are normally produced and driven again to the corresponding separation system.

The same heuristics as in organic processes can be applied when choosing the separation task. Crystallization and precipitation operations, followed by solid-liquid separations (sedimentation or filtration, by example) are used in many cases. In inorganic processes there are normally not a great number of separations and the sequencing problem is not difficult. In all cases, heuristics such as the removal of corrosive and dangerous species first, removal of the most abundant species, making difficult separations last, etc., can be applied.

The last step in process synthesis is the integration of operations. In the inorganic processes, the same general criteria are valid as in organic processes.

It can thus be concluded that the student's education in process synthesis can consist of transmission of the necessary experience together with heuristics or rules-of-thumb. This instruction in process synthesis can be an advantageous substitute for the exhaustive descriptions of chemical processes which is given to students in subjects such as industrial chemistry.

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LETTER: Langmuir's Isotherm

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And from Eqs. (4) to (6)

$$\begin{aligned}\theta_j &= K_j c_j \theta_{\text{free}} = K_j c_j \left(1 - \sum_{i=1}^m \theta_i \right) \\ &= K_j c_j \left(1 - \frac{\theta_j}{K_j c_j} \sum_{i=1}^m (K_i c_i) \right) = K_j c_j - \theta_j \sum_{i=1}^m K_i c_i\end{aligned}$$

Solved for θ_j

$$\theta_j = \frac{K_j c_j}{1 + \sum_{i=1}^m (K_i c_i)}$$

The concentration of j on the adsorbent is proportional to the surface fraction occupied by j , so that

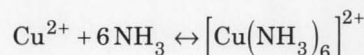
$$q_j = k_j \theta_j = \frac{k_j K_j c_j}{1 + \sum_{i=1}^m (K_i c_i)} \quad (7)$$

where k_j is another constant. This is of the form of Eq. (1), with $k_j K_j$ corresponding to a_j and the K_i to the b_i .

This derivation also gives the same result as Langmuir's for adsorption of a dissociating molecule, for instance, of H_2 as 2 H occupying two sites.

Langmuir-type adsorption is seen to result from "ideal" thermodynamic behavior, that is, from the absence of any specific interactions that would result in activity-coefficient corrections or call for the definition of additional species. This is a more germane reason than are the adsorption and desorption rates. That adsorption *equilibrium* has a basis in thermodynamics will be easier for the student to accept and will convey better insight into why many adsorbents behave in this manner, and why some do not.

When I went to school, more years ago than I care to count, textbooks still derived the mass-action law for reactions with the kinetic argument of equal forward and reverse rates at equilibrium—one of them even with the reaction



postulating a single-step mechanism with hepta-molecular formation and decay into seven fragments! Happily, we have long outgrown such nonsense and have put the mass-action law for reactions on a sounder basis. Is it not time that we accord the Langmuir isotherm the same courtesy?

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2. For instance, see Fogler, H.S., *Elements of Chemical Reaction Engineering*, Prentice-Hall, Englewood Cliffs, NJ, p. 241 (1986) □

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