

This Week's Citation Classic

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Myers A L & Prausnitz J M. Thermodynamics of mixed-gas adsorption.
AIChE J. 11:121-7, 1965.
[University of California, Berkeley, CA]

Adsorption has recently become more competitive with distillation and extraction as a means of separating gaseous and liquid mixtures. Feasibility of adsorptive separation can be estimated by the ideal adsorbed solution (IAS) approach, which was proposed in 1965. [The SC²® indicates that this paper has been cited in over 115 publications since 1965.]

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"This paper was written in 1963 while I was a graduate student at Berkeley. It was a time of rapid growth for chemical engineering education, and many fellow students (Douglas Benion, John Berg, Charles Eckert, John Friedly, Joe Goddard, Edward Grens, Robert Madix, John Newman, John O'Connell, Fred Shair, and Darsh Wasan) moved into teaching careers after graduation. The intellectual environment was lively and stimulating, and I received many helpful suggestions from classmates, especially Neil Dougharty and Alan Pasternak.

"My research adviser and coauthor was John Prausnitz, who had suggested adsorption for a thesis topic two years earlier. This was a timely choice because of a series of advances made during the 1950s and early-1960s. Terrell Hill¹⁻³ had published a classic series of papers on the thermodynamics and statistical mechanics of adsorption. At the same time, George Halsey, Jr., and his co-workers, including William Steele,⁴ had developed the concept of surface excess and were analyzing their high-precision isotherms for graphitized carbon in terms of gas-solid and gas-gas intermolecular potentials. Then, in 1962, Young and Crowell⁵ wrote a book on physical adsorption which summarized these and other developments.

"My thesis on adsorption was published as three papers,^{6,7} and the mixture work was the least theoretical part. Hill's papers had impressed upon me the fundamental role of spreading pressure in adsorption, and it was my good fortune to be the first chemical engineer to work on the thermodynamic aspects of adsorption. Previous research was directed almost exclusively toward adsorption of pure gases, usually by surface chemists unfamiliar with the solution thermodynamics and excess functions developed for liquid mixtures. The key step in this paper was the recognition that the Gibbs adsorption isotherm was similar in substance and form to the more familiar Gibbs-Duhem equation of vapor-liquid equilibrium. There was no flash of insight, unfortunately; it was more a matter of trying to organize and simplify pages of lengthy and often abstruse thermodynamic equations. But once I saw the connection between gas-solid and vapor-liquid equilibrium, it was a simple and in fact obvious step to write down the basic equations pertinent to adsorption of mixtures, by analogy.

"After developing the equilibrium relations in terms of excess functions, we postulated Raoult's law for mixture equilibrium. This idea was prompted by experimental data for adsorption of nitrogen and oxygen on anatase by James Arnold,⁸ who applied Raoult's law individually to each site in connection with the Brunauer-Emmett-Teller (BET) theory. We went further and proposed that the entire surface layer behaves as an ideal solution, in order to simplify the equations. Prausnitz and I considered this to be a naive assumption, but it has proven to be remarkably accurate for high-area commercial adsorbents and has come to be known as the method of ideal adsorbed solution (IAS).

"This paper is frequently cited because IAS has become a standard for comparison: both experimental data and new theories are usually compared to IAS because of its thermodynamic consistency. Also, it gave engineers a practical technique for estimating mixture equilibrium. In recent years, the IAS method has been successfully applied to mixtures of organic solutes adsorbed from aqueous solution."⁹

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5. Young D M & Crowell A D. *Physical adsorption of gases*. London: Butterworths, 1962. 426 p.
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