

tion, especially when the seeding is in depth; the reaction should have set in almost at once. Worse yet, since the winds were near 180 kilometers per hour, all the material should have traveled a great distance in 20 minutes. At the 15-kilometer radius, for instance, the seeded air should have moved about halfway around the storm, since, in the southwest sector, the winds did not exceed 150 kilometers per hour (80 knots). Therefore there is no obvious reason for connecting the radar fadeout with the seeding. Yet the transformation in the observations of the 10-centimeter radar was spectacular, and veteran observers of radar in hurricanes have stated that they have not found such marked changes on other occasions.

Changes in the wind field were small and probably within the range of normally occurring microfluctuations, but

this finding is without relevance, since only one set of generators was dropped. The atmosphere is a rather inert medium, and large-scale circulations respond slowly to impressed changes. Enormous instantaneous infusions of energy, such as are supplied by hydrogen bombs, have not been observed to affect broadscale flow features of the troposphere. The energy disperses rapidly, and only a traveling pressure wave can be followed. In considering ways to make an impact on a weather system as large as a hurricane, where the earth's rotation is involved, one must think in terms of continuing operations, with a minimum duration of 12 hours.

In summary, the whole experiment leaves us without obvious concrete results but with more curiosity than ever, and with some feeling of encouragement. It is safe to predict that future

experiments will be watched by the meteorological profession, and by the public, with more than casual interest (12).

#### References and Notes

1. V. Bjerknes *et al.*, *Physikalische Hydrodynamik* (Springer, Berlin, 1933).
2. G. E. Dunn, *Monthly Weather Rev.* **68**, 303 (1940).
3. H. Riehl, *Tropical Meteorology* (McGraw-Hill, New York, 1954).
4. ———, *Science* **135**, 13 (1962).
5. ———, *Univ. Chicago Misc. Repts.* No. 24 (1948).
6. M. Yanai, *J. Meteorol. Japan*, **39**, 187 (1961).
7. The practice of assigning girls' names to hurricanes started during World War II as an outgrowth of G. R. Stewart's *Storm* (Random House, New York, 1941). After 20 years, a change might be welcomed.
8. V. J. Schaefer, in *Compendium of Meteorology*, T. F. Malone, Ed. (Am. Meteorol. Soc., Boston, 1951).
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11. R. H. Simpson, M. R. Ahrens, R. D. Decker, "National Hurricane Research Project Report No. 60," *U.S. Weather Bureau Publ.* (1963).
12. A second experiment was performed on 23 August 1963.

## The Potential Theory of Adsorption

Authority in science has its uses and its dangers.

Michael Polanyi

Since 1948, when I retired from the professional pursuit of science to take up philosophy, occasional reports have reached me that my theory of adsorption, which hitherto had been rejected, was gradually gaining acceptance. Assuming that this outcome is no longer in doubt (1), I think it worthwhile to look back on the reasons why this fairly simple matter has so long been left undecided. The story also throws light on an interesting aspect of the scientific method.

I wrote my first paper on adsorption 49 years ago; it was published in 1914. In it I assumed (i) that the adsorption of gasses on solids is due to an attraction that derives from a potential which is uniquely determined by the spatial

position of the gas molecule and therefore independent of the presence of any other molecules in the field of the adsorption potential; and (ii) that, when subject to the field of adsorption, the gas behaves in accordance with its normal equation of state. When compressed to its normal vapor density, it condenses to a liquid.

These principles were first fully developed in a paper published in 1916, which also supplied a wide range of experimental verification, as follows. From a complete adsorption isotherm of a vapor, a distribution of the adsorption potential was derived, in the form  $\epsilon = f(\phi)$ ,  $\epsilon$  being the adsorption potential and  $\phi$  the space enclosed by the level having this potential, and from this adsorption-potential curve all other measured isotherms were computed and found to agree

with the theory. This result was confirmed later in a number of papers by my pupils and by other authors (2).

The result was impressive. Herbert Freundlich, then the most authoritative writer on this subject, gave a full account of my theory in the next edition of his *Kapillarchemie*, published in 1922. He told me, "I am heavily committed now to your theory myself; I hope it is correct."

Actually, his words already expressed an uneasiness, and soon my theory was almost universally rejected. How did this happen?

During the very years in which the theory was born, there occurred a dazzling series of insights into the nature of things. Debye's discovery of fixed dipoles, Bohr's atomic model, and the ionic structure of sodium chloride found by W. H. Bragg and W. L. Bragg, established the pervasive function of electrical forces in the architecture of matter. It seemed obvious that, in consequence, cohesive forces must be explained by electrical interaction. A number of theories were put forward on these lines. Keesom suggested an electrostatic interaction of fixed quadrupoles; Debye, an interaction of quadrupoles with induced dipoles. Kossel's attempt to explain all chemical bonds as attraction between positive and negative ions also belongs to this period.

This view of atomic forces made my theory of adsorption untenable.

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Electrical interactions could not be derivable from a spatially fixed potential; they would be screened off by the presence of other molecules in the field.

The weight of these theoretical objections was greatly increased by three experimental claims put forward by Irving Langmuir in the years 1916 to 1918. (i) Langmuir reported that the adsorption of gasses on mica surfaces reached saturation with the formation of an adsorbed layer of less than monomolecular strength. (ii) He claimed that isotherms could be accounted for by an equation that has since been known as "Langmuir's isotherm"—an equation in which it is presupposed that molecules are adsorbed at scattered centers by forces that render attraction between adsorbed molecules negligible. (iii) Langmuir proved by beautiful experiments that surface layers on water are monomolecular and that their structure is determined by electrostatic interaction with the underlying water. For this work he was awarded the Nobel prize.

All this evidence seemed to bear out the picture of short-range electrical forces, or valences, originating at discrete points of the atomic lattice forming the wall—a picture which would render my theory of adsorption untenable.

I myself was protected for a while against any knowledge of these developments by serving as a medical officer in the Austro-Hungarian Army, from August 1914 to October 1918, and by the subsequent revolutions and counter-revolutions that lasted until the end of 1919. Members of less-well-informed circles elsewhere continued to be impressed for some time by the simplicity of my theory and its wide experimental verifications. But its downfall had become inevitable.

The turning point came when I was invited by Fritz Haber to give a full account of my theory in the Kaiser Wilhelm Institute for Physical Chemistry, in Berlin. Einstein was especially invited to attend my lecture. Some scientists present who had not yet fully accepted the electrical concept of interatomic forces congratulated me on "the flood of light" I had thrown on the subject, but Einstein and Haber decided I had displayed a total disregard for the scientifically established structure of matter. Professionally, I survived the occasion only by the skin of my teeth.

However, my belief in my theory was quite unshaken, and I proceeded to undertake a series of experiments with a view to proving its validity. These experiments offered good supporting evidence for the theory, even though there were some systematic deviations from it. These I attributed to the fact that the surface tension of the very thin, *possibly* monomolecular, adsorbed layer vitiates to some extent the assumption that the adsorbed substance behaves according to the equation of state for the substance observed in bulk. Once more I reported my results to a meeting presided over by Haber in Berlin. When I finished, Haber declared that, by my admission of systematic deviations from the theory and of the possibly monomolecular thickness of the adsorbed layer as an explanation of these deviations, I had actually given up my theory. I had, of course, done nothing of the kind, but I had certainly become quite isolated in my belief in it, at least from the leading scientists of the time (3).

### Refutation

And yet deliverance was approaching. In 1930, F. London put forward a new theory of cohesive forces, based on quantum mechanical resonance between the polarization of electronic systems. I immediately fired the following question at London: "Are these forces subject to screening by intervening molecules? Would a solid acting by these forces possess a spatially fixed adsorption potential?" London carried out the computation, and we published the result jointly (in 1930): Adsorptive forces behave exactly in accordance with the assumptions of my theory. Having found this, we inferred that the adsorption potential of a solid wall decreases with the third power of the distance from the wall. (I refer to this inference hereafter as the "inverse third power law.")

The following year I was invited to give an introductory lecture before the Faraday Society on the subject of adsorption. In this lecture I showed that application of the inverse third power law to determine adsorption potential for a wedge-shaped crevice yields  $\epsilon = f(\phi)$  curves of the characteristic type observed for charcoal.

I thought I had now won the battle I had fought for 15 years. But my paper before the Faraday Society (4)

actually made no impression. It seems that by this time the opinion that my theory was false had hardened to a point where the reasons for which it had been rejected were forgotten. Hence my refutation of these objections had no effect.

There were, of course, still some objections to be met. To Langmuir's claims, developed along the lines I have mentioned, new evidence had been added, by the adsorption of cesium vapor on tungsten. Attention was also drawn from adsorption by cohesive forces to chemisorption, because of its bearing on heterogeneous catalysis, even though it rarely produces equilibria for the study of adsorption isotherms. In addition, the suitability of my experimental material was questioned on the grounds that it was porous, with unknown irregular surface configurations. These objections have continued to exercise some influence up to the present.

However, Langmuir's extrapolation of his isotherms on mica (from observations made in 1917) was soon to prove erroneous: saturation was found to take place at a multimolecular thickness of the adsorbed layer. That the Langmuir isotherm itself is theoretically false still seems to be insufficiently appreciated today. It is not applicable to any adsorption by cohesive forces, for the differences in the molecular energy of such adsorption along a solid surface are very small and can never outweigh the cohesive energy of the adsorbed molecules. The Langmuir isotherm might conceivably be applicable to chemisorption, when chemisorption is reversible. But the only instance I know of in which it clearly applies is the deposition of cesium cations on a negatively charged tungsten surface, a very untypical case of adsorption. To represent the Langmuir isotherm as a proper approximation to the adsorption equilibrium is therefore misleading. The formula should be dropped altogether.

Work in recent years has shown that the isotherm of adsorption on plane surfaces can be derived, beyond the point at which the first one or two layers of molecules are adsorbed, from an adsorption potential that obeys the inverse third power law, while the part of the isotherm that corresponds to the deposition of the first layers does not obey my theory. This follows, in my view, from the fact that the surface tension of the adsorbed layer keeps it

from behaving in accordance with the normal equation of state at the early stages of adsorption. Confirmation of the inferred inverse third power law for plane surfaces is a beautiful experimental achievement, yet porous adsorbents retain the advantage that the adsorbed layer is accumulated on them in such a way that surface tension is reduced, and makes the normal equation of state applicable to the entire observed isotherm. The discrediting of my verification of my theory on the grounds that the verification was based on experiments with porous adsorbents proved to be unjustified.

This historical survey may be of interest to scientists puzzled by the fact that the acceptance of the correct theory of adsorption was delayed by almost half a century; but I think its main interest lies in the bearing of the story on the scientific method.

### Bearing on the Scientific Method

The first point to mention is the fact that I would never have conceived my theory, let alone have made a great effort to verify it, if I had been more familiar with major developments in physics that were taking place. Moreover, my initial ignorance of the powerful false objections that were raised against my ideas protected those ideas from being nipped in the bud. Later, by undertaking the labor necessary to verify my theory, I became immune to these objections, but I remained powerless to refute them. My verification could make no impression on minds convinced that it was bound to be specious. Since electrical forces could not produce an adsorption potential of the kind I was postulating, and since no principle was conceivable at the time which could account for such an adsorption potential, Langmuir's claims supporting the then current view of matter were firmly accepted, though they were false (or irrelevant to adsorption on solid surfaces), and my evidence was rejected unexamined, though it was valid. I could do nothing about it.

### Suppression of Evidence

Could this miscarriage of the scientific method have been avoided? I do not think so. There must be at all times a predominantly accepted scien-

tific view of the nature of things, in the light of which research is jointly conducted by members of the community of scientists. A strong presumption that any evidence which contradicts this view is invalid must prevail. Such evidence has to be disregarded, even if it cannot be accounted for, in the hope that it will eventually turn out to be false or irrelevant.

I shall repeat here some comments that I made in an earlier essay on the way in which current views of plausibility properly serve to suppress evidence that runs counter to them (5). Observations which can be interpreted as a transmutation of chemical elements frequently occur in the laboratory. But published claims, by reputable investigators, of having achieved transmutation appear only at times when the possibility of such a process is for some reason considered plausible. Such was the case when suddenly, under the stimulus of Rutherford's and Soddy's discovery of radioactive transmutations (1902-3), careful observers made a series of erroneous claims that they had achieved a transmutation of elements. A. T. Cameron (1907) and Sir William Ramsay (1908) announced the transformation of copper into lithium as a result of the action of  $\alpha$ -particles.

In 1913 Collie and Patterson claimed that they had formed helium and neon by electric discharge through hydrogen. After these claims had been disproved, no new ones were made until 1922, when as a result of the discovery, made 3 years earlier by Rutherford, of certain forms of artificial transmutation, there was a new wave of similar claims based on erroneous evidence. The transmutation of mercury into gold under the effect of electric discharge was reported independently by Miethe and Stammreich in Germany and Nagaoka in Japan. Smits and Karssen reported the transformation of lead into mercury and thallium. Paneth and Peters claimed that hydrogen had been transformed into helium under the influence of a platinum catalyst. All these claims had to be abandoned in the end; the last was given up in 1928. A year later came the establishment of the theory of radioactive disintegration, which showed that these attempts to transform elements had been futile. Since then, up to this time I have seen no such claims published, although evidence of transformation of the kind

put forward by Ramsay, Paneth, and others must be turning up all the time. It is disregarded and would not be accepted for publication, because it is no longer considered sufficiently plausible. Remember, also, D. C. Miller's observations contradicting the result of the Michelson-Morley experiment. They were properly set aside for a period of about 50 years, though they were not explained and shown to be erroneous until 1955 (6).

I am making, therefore, no complaint about the suppression of my theory for reasons which must have seemed well founded at the time, though they have now been proved false. It is perhaps more difficult to understand why more than 15 years passed after the presentation of my paper of 1932, in which the original objections had been proved unfounded, before the rediscovery and gradual rehabilitation of the theory set in. I suppose so much confusion was left over from the previous period that it took some time for scientists to take cognizance of the new situation, and that meanwhile my own work, which had been so long discredited, remained suspect. If the problem had been more important, this period of latency would have, no doubt, been shorter.

The dangers of suppressing or disregarding evidence that runs counter to orthodox views about the nature of things are, of course, notorious, and they have often proved disastrous. Science guards against these dangers, up to a point, by allowing some measure of dissent from its orthodoxy. But scientific opinion has to consider and decide, at its own ultimate risk, how far it can allow such tolerance to go, if it is not to admit for publication so much nonsense that scientific journals are rendered worthless thereby.

Discipline *must* remain severe and *is* in fact severe. I doubt that I could have got my theory of adsorption passed by the referees of any scientific journal had I presented it 5 years later than 1916. I was lucky enough to profit by the relative ignorance of referees in 1916, and also by the complete ignorance of the professor of theoretical physics at the University of Budapest, who accepted the substance of my theory as a Ph.D. thesis in 1917 (may his departed spirit forgive me these ungrateful remarks!).

Even so, the opposition to my theory would have cut off any hope I had of a scientific career—on which, having

left medicine, I was embarking belatedly—had I not done other scientific work that brought me recognition which outweighed the discredit brought upon me by my theory of adsorption.

Even as professor of physical chemistry at the Victoria University of Manchester, I was unable to teach my theory. Undergraduates would have expected to be examined on it. But examinations were set and marked by a committee that included an external examiner and members of the teaching staff junior to myself. I could not undertake to force on them views totally opposed to generally accepted opinion. A system of collegiate examinations severely curtails the teaching of views that conflict with currently dominant scientific opinion.

### Orthodoxy and Dissent

I repeat here that I am not arguing against the present balance between the powers of orthodoxy and the rights of dissent in science. I merely insist on acknowledgment of the fact that the scientific method is, and must be, disciplined by an orthodoxy which can permit only a limited degree of dissent, and that such dissent is fraught with grave risks to the dissenter. I demand a clear recognition of this situation for the sake of our intellectual honesty as scientists, and I charge that this situation is not recognized today but is, on the contrary, obscured by current declarations about science. Take this by Bertrand Russell (7):

The triumphs of science are due to the substitution of observation and inference for authority. Every attempt to revive authority in intellectual matters is a retrograde step. And it is part of the scientific attitude that the pronouncements of science do not claim to be certain, but only

the most probable on the basis of present evidence. One of the great benefits that science confers upon those who understand its spirit is that it enables them to live without the delusive support of subjective authority.

Such statements obscure the fact that the authority of current scientific opinion is indispensable to the discipline of scientific institutions; that its functions are invaluable, even though its dangers are an unceasing menace to scientific progress. I have seen no evidence that this authority is exercised without claims of certainty for its own teachings. In any case, it is a mistake to assume that it is easier to justify a scientific opinion that merely makes claims of probability than one that makes claims of certainty. Both express a commitment, and to this extent both must go beyond the evidence.

The instance of the miscarriage of science of which I have told the story may not have been important in itself, but it makes me ponder the perils of a particular dangerous mode of scientific explanation. The physicists of the period from 1912 to 1930 considered it as established beyond reasonable doubt that only electrical forces could account for intramolecular attraction. Arguments for the insufficiency of this explanation were rejected as unscientific, because no other principles of molecular interaction appeared conceivable. This reminds me of the impatience with which most biologists set aside today all the difficulties of the current selectionist theory of evolution, because no other explanation that can be accepted as scientific appears conceivable. This kind of argument, based on the absence of any alternative that is accepted as scientific, may often be valid, but it seems to me the most dangerous application of scientific authority.

### References and Notes

1. I am relying for this assumption on the following surveys: M. M. Dubinin, "The potential theory of adsorption of gasses and vapors for adsorbents with energetically non-uniform surfaces," *Chem. Rev.* **60**, 235 (1960), and R. S. Hansen and C. A. Smolders, "Colloid and surface chemistry in the mainstream of modern chemistry," *J. Chem. Educ.* **30**, 167 (1962).
2. In my paper of 1914 I calculated from the adsorption isotherm of a vapor the potential energy of an adsorbed molecule as a function of the amount adsorbed, which I identified with the distance from the surface of the adsorbent, assumed to be plane. (The fact that the adsorbent was actually porous did not affect the predictions of the theory; in the paper of 1916 I introduced the concept that the volume enclosed by a potential surface is the variable on which the potential depends.) The term *Adsorption potential* was first introduced by Eucken [*Verhandl. Deut. Phys. Ges.* **16**, 345 (1914)] a few months before publication of my paper of 1914. Eucken computed, from a hypothetical formula for the decrease of the adsorption potential with the distance from a plane adsorbent, the temperature dependence of the linear part of the adsorption isotherm. This procedure was erroneous in four respects. (i) Insufficient account was taken of the porosity of the adsorbents; such porosity profoundly alters the potential distribution relative to that on a plane surface. (ii) The inclination of the hypothetical linear part of the isotherms was assessed from the initial slope of a curved isotherm taken from the literature—a procedure which was not justifiable. (iii) The procedure was self-contradictory, for the ideal gas laws were applied to conditions in which, according to the theory itself, the ideal gas laws could not possibly hold. (iv) The hypothetical formula used for the adsorption potential of a plane solid wall was incorrect. Eight years later, Eucken [*Z. Elektrochem.* **28**, 6 (1922)] attacked my theory while modifying his own assumptions to include some of those I had made.
3. One of the papers published in 1928 [*Z. Phys. Chem.* **132**, 321 (1928)] lent strong support to my theory from a new angle. It showed that, below the melting point of a substance, the quantity adsorbed at saturation steadily increases with rising temperature up to the melting point. The nature and magnitude of this effect could be derived from the fact, assumed in my theory, that the adsorbed layer is an amorphous modification of the adsorbed substance. This paper seems to have gone entirely unnoticed.
4. M. Polanyi, *Trans. Faraday Soc.* **28**, 316 (1932).
5. —, *Science, Faith and Society* (Oxford Univ. Press, Oxford, 1946), pp. 75–76.
6. See M. Polanyi, *Personal Knowledge* (Univ. of Chicago Press, Chicago, 1959), p. 13; for other cases, see *ibid.*, p. 276, and M. Polanyi, *Logic of Liberty* (Univ. of Chicago Press, Chicago, 1951), p. 17.
7. B. Russell, *The Impact of Science on Society* (Allen and Unwin, London, 1952), pp. 110–111.