Hall's Notes and Queries

NQ12

Isothermal history

In this NQ, I give a brief account of the rather complicated history of the equations used to describe sorption isotherms. It captures some background work done for two new papers with colleagues on water vapour sorption in building physics and inorganic materials.

Langmuir

In 1914, Irving Langmuir,[1] at General Electric in Schenectady, started investigations of the adsorption of simple gases on plane surfaces such as mica, glass and platinum. This led to a paper [1] in 1918 in which he derives the mathematical statement of the so-called Langmuir adsorption isotherm.[2] Langmuir argues that "a large number of experiments … prove that true adsorbed films do not exceed

---

[1] Langmuir received the Nobel prize for Chemistry in 1932 for "for his discoveries and investigations in surface chemistry".

[2] Langmuir's simple monolayer isotherm equation was first given without derivation in 1916 [2]. Strictly the priority for the first isotherm equation with a theoretical basis should be given to Michael Polanyi, who published papers on adsorption in 1914 and 1916. Polanyi's isotherm, based on potential energy rather than kinetic arguments, was widely considered to be wrong and had little influence, for reasons set out by Polanyi in an apologia in 1963 [3]. An earlier isotherm, now generally called the Freundlich isotherm [4], was originally empirical [5]. It is still used for adsorption from solution but much less for gas/vapour sorption.

one molecule in thickness.” The Langmuir isotherm,[3] as generally presented today, deals with the formation of *monolayers* of simple (usually permanent) gases on flat, homogeneous surfaces. Langmuir derived the isotherm by kinetic arguments.

Brunauer, Emmett and Teller[4]

Much later, in 1938, Stephen Brunauer, Paul Emmett and Edward Teller [6] derived a different isotherm equation, also by kinetic arguments. The BET isotherm equation allows for the formation of multiple molecular layers of adsorbate (gas or vapour) on the surface of the solid adsorptive. The BET equation has been influential in providing a two-parameter model that is widely successful in representing the sorption behaviour of many systems, at least if high relative pressure data are excluded.

The greater importance of the BET equation is that it has long been the basis of the standard method of determining the surface areas of solid materials, since the BET parameter n_m is the amount adsorbed at complete monolayer coverage. Given some sort of agreed value for the area occupied by a single adsorbate molecule, a surface area can be estimated [7].

Although Langmuir was mainly concerned with monolayer adsorption, his 1918 paper [1] does contain an analysis of *multilayer* adsorption (Langmuir’s ”Case VI”) that is the same as the BET equation.

---

[3] The isotherm equations themselves are set out at the end of this NQ.

[4] Edward Teller’s appearance in this story is surprising. As a refugee Hungarian atomic physicist, he found himself briefly at George Washington University in 1937, where he met Stephen Brunauer. In this interview, he makes it clear that Brunauer had the theory all wrong until he, Teller, sorted it out.

This was first noted by D C Jones [8], and later by Edward Guggenheim [9].

The kinetic basis of the Langmuir and BET isotherms was persistently criticised by proponents of the statistical thermodynamic theory of adsorption.[5] Ralph Fowler rederived the Langmuir isotherm by such statistical arguments in 1935 [11, 12], and then Terrell Hill in 1946 similarly derived the BET equation. In 1966 Guggenheim [9] said, sternly, of both Langmuir and BET that ″the original derivations … depended on kinetic considerations which are entirely irrelevant to equilibrium conditions″, and even said that ″recently published statistical derivations are unnecessarily complicated″, presumably aiming at Hill.

Frenkel, Halsey and Hill

In 1946,[6] Yakov Frenkel [14] published an isotherm equation for multilayer adsorption quite different in form from the BET equation. The same equation was derived independently by George Halsey [15] in 1948, and then using different methods by Hill [16] in 1949. It is clear that neither Halsey nor Hill was aware of Frenkel's earlier work when they published their papers, although Hill acknowledges Halsey's. Later, in his 1952 review of adsorption theory [17], Hill recognised Frenkel's claim to priority, and for the first time brought the three equations together as the Frenkel-Halsey-Hill or FHH isotherm.

---

[5] The kinetic theory of adsorption was most elaborately set out by De Boer in his book of 1953 [10].

[6] Frenkel's derivation of the Frenkel isotherm can be dated to around 1943-1944, when he completed the ms of his book. The book was written in the Soviet Union in difficult wartime circumstances and not published until 1946 [13].

Guggenheim, Anderson and de Boer

The third important isotherm equation emerged from dissatisfaction with the BET equation at high relative pressures. Independent work by Robert Anderson [18] in 1946, de Boer [10] in 1953 and Guggenheim [9] in 1966 all yielded the same new isotherm, although by different arguments. This may be regarded as an ′extended′ BET equation, since it introduces an extra free parameter that when set equal to 1 gives back the BET equation.

The three separate derivations were only brought together in 1981 by C van den Berg[7] [19], who showed that they were essentially the same and for the first time called the common equation the Guggenheim-Anderson-de Boer[8] (or GAB) isotherm. It is not clear why van den Berg gave precedence to Guggenheim, when it would have been appropriate to give priority to Anderson. Probably van den Berg liked the rigour of Guggenheim's statistical mechanical theory which he set out at length in his thesis.[9]

---

[7] Van den Berg's PhD under the supervison of Hans Lyklema, the distinguished colloid chemist, was carried out at Wageningen University, a leading international research centre for food science. The work was influential in that field in promoting the use of the GAB isotherm for water vapour sorption.

[8] The GAB isotherm is occasionally referred to as the Brunauer-Skalny-Bodor (BSB) isotherm, after it was proposed by these authors in 1969 [20]. They acknowledged that it was identical to the Anderson isotherm, and therefore to what was later called the GAB isotherm.

[9] Guggenheim's elegant analysis in [9] is clear and simple, once one accepts the partition function formalism. It leads to what may be called a *generalised* multilayer isotherm equation, based on the same assumptions about the nature of the surface and the adsorbed multilayer that were made by Langmuir. With various different constraints on the parameters, Guggenheim's equation reduces to the GAB, or the BET or the Langmuir monolayer isotherm.

Comment

From Langmuir's early work on monolayers of simple gases on flat homogeneous surfaces we have come now to the extended BET equation for multilayers of more complex gases and vapours, often on heterogeneous surfaces. The period of greatest activity was from about 1946 until about 1952. Now some 75 years later, the GAB and FHH isotherms remain widely used. Both have a theoretical basis (or several!) and are not purely phenomenological, although the interpretation of the parameters is often little more than empirical. Many users these days are looking for a robust description of adsorption/desorption behaviour and are perhaps not overly concerned with molecular interpretations.

Isotherms in building physics and materials

In what follows, I identify a few notable contributions to sorption studies in this field. It is not comprehensive, but may provide a useful timeline. Essentially all investigations deal with water-vapour sorption.[10]

- In their massive 1948 study [21] of the physical properties of hardened cement paste,[11] Powers and Brownyard report extensive work on "water fixation". This includes much experimental work on water vapour sorption, using novel laboratory equipment of high accuracy. They make use of the BET equation for data below 40 percent RH. Of course, the interpretation of the measured isotherms is far from straightforward, since

---

[10] Apart of course for the extensive use of nitrogen-adsorption BET methods to measure the specific surface area of materials.

[11] Each time I dip into this I am stunned by its extraordinary quality: the range, novelty and skill of their experiments, the sanity of their judgments, the precision of their reporting.

they reflect a combination of chemical hydration and classical adsorption, with nanoscale capillarity effects as well. Powers and Brownyard undertook these studies for scientific rather than technical reasons.

- In 1966, Annanias Tveit [22] at the Norwegian Building Research Institute published water-vapour sorption isotherm data on 48 construction materials, mostly organic, but including several brick, mortar and concrete materials. There was however no attempt to apply an isotherm equation, and no work outside the building research field was cited.

- Another large set of water-vapour sorption isotherms was compiled in 1986 by Kurt Hansen [23] at the Danish Technical University. This catalogue of sorption isotherms has been widely cited in the building physics literature. The 119 materials included are diverse, with about 46 inorganic construction materials such as brick, cement, mortar, concrete and plaster. Data are taken from earlier publications. Hansen fitted all data to an isotherm equation attributed to Per Freiesleben Hansen [source document not found][12]. It is described in [23] as empirical, although it closely resembles the FHH isotherm.

- With only a few exceptions, the isotherm equations used in the building physics and materials field are empirical and without theoretical basis. The Freiesleben Hansen isotherm is used by Kumar Kumaran [24] in the 1996 IEA report on heat and moisture modelling, and then by Černý and Rovnaníková [25]. Different empirical isotherm equations are given by Hartwig

---

[12] Cited in [23] as P Freiesleben Hansen (1985), 'Coupled moisture/heat transport in cross sections of structures'. Beton og Konstruktionsinstituttet (BKI). It has not yet been possible to find a copy of this publication

Künzel [26] in a 1995 publication on heat and moisture modelling.

The main exceptions to the use of empirical equations are in studies of water vapour sorption in hardened cement pastes. Following Powers and Brownyard, we have for example [27] using an extended BET isotherm, and [28] using GAB and FHH isotherms. However, as already noted, cement pastes are unusual materials in which simple water vapour adsorption is overlaid with strong effects of chemical hydration and nanoscale capillarity effects, as discussed, for example in [29, 30].

- The use of the GAB and FHH isotherm equations in building physics was long delayed. A notable contribution using both was published only in 2012 by Pavlik and his co-authors [31].

Summary of isotherm equations

For reference, here are the isotherm equations mentioned in this NQ, all expressed in a common notation and in a form appropriate for water vapour sorption. Here n is the amount (mol) adsorbed, n_{m} the amount adsorbed in forming a monolayer, p the gas or vapour pressure, p_0 the saturated vapour pressure, and where appropriate $H = p/p_0$, the fractional humidity, RH/100.

- **Freundlich**

$$n = k_0 p^{1/q} \tag{1}$$

where k_0, q are the Freundlich parameters.

- **Langmuir**
$$\frac{n}{n_\mathrm{m}} = \frac{k_1 p}{1 + k_1 p} \tag{2}$$
where k_1 is the Langmuir constant; the equation is applicable only for $n \leq n_\mathrm{m}$, monolayer coverage and below.

- **BET**
$$\frac{n}{n_\mathrm{m}} = \frac{c_2 H}{(1 - H)[1 + H(c_2 - 1)]} \tag{3}$$
where c_2 is the BET parameter.

- **GAB**
$$\frac{n}{n_\mathrm{m}} = \frac{c_3 k_3 H}{(1 - k_3 H)[1 + k_3 H(c_3 - 1)]} \tag{4}$$
where c_3, k_3 are the GAB parameters.

- **FHH**
$$\frac{n}{n_\mathrm{m}} = \left[-\frac{b}{\ln H}\right]^{1/s} \tag{5}$$
where b, s are the FHH parameters. The FHH isotherm is intended for multilayer adsorption only, $n \geq 2n_\mathrm{m}$ say.

- **Freiesleben Hansen**
$$\frac{n}{n_\mathrm{h}} = \left[1 - \frac{\ln H}{A}\right]^{-1/r}. \tag{6}$$
where A, r are the Hansen isotherm parameters, and subscript h denotes the ″maximum hygroscopically bound water by adsorption″ [23].

Comment. The Freiesleben Hansen isotherm equation as originally written by K K Hansen in [23] is
$$H = \exp\left[A - \left(1 - (u/u_\mathrm{h})^{-r}\right)\right], \tag{7}$$

where H, r are used for Hansen's original symbols ϕ, n, and u denotes the fractional water content by weight. Rearranging this and using $u/u_\mathrm{h} = n/n_\mathrm{h}$ gives Eqn 6.

It is a useful feature of Eqn 7 that as $H \to 1$, $u \to u_\mathrm{h}$. This therefore provides a clear definition of the maximum hygroscopically adsorbed water. Furthermore, as $H \to 0$, $u \to 0$.

A source of confusion is the supplementary relation given by Hansen [23], $A = (u_\mathrm{n}/u_\mathrm{h})^r$. The quantity u_n, described as the "non-evaporable water content", is not found from an independent experimental measurement, but is simply determined by the regression parameters A and u_h. But from Eqn 7, we see that $u = u_\mathrm{n}$ when $H = H_\mathrm{n} = \exp(A - 1)$. Typically H_n has a value in the range 0.35–0.4, close to $\exp(-1)$, so that u_n certainly cannot be described as the non-evaporable water content. u_n appears to have no physical or practical significance.

For many of Hansen's materials at $H \leqslant 0.9$, the quantity $|(\ln H)/A| \gg 1$, so that

$$u = \left[-\frac{A'}{\ln H}\right]^{1/r} \tag{8}$$

where $A' = Au_\mathrm{h}^r$. This closely resembles the FHH isotherm, Eqn 5.

References

[1] Irving Langmuir. 'The adsorption of gases on plane surfaces of glass, mica and platinum.' In: *Journal of the American Chemical Society* 40 (1918), pp. 1361–1403.

[2] Irving Langmuir. 'The constitution and fundamental properties of solids and liquids. Part I. Solids.' In: *Journal of the American Chemical Society* 38 (1916), pp. 2221–2295.

[3] Michael Polanyi. 'The potential theory of adsorption: Authority in science has its uses and its dangers.' In: *Science* 141 (1963), pp. 1010–1013.

[4] Herbert Freundlich. *Kapillarchemie*. Leipzig: Akademische Verlag, 1909.

[5] Charles H Giles. 'The history and use of the Freundlich adsorption isotherm'. In: *Journal of the Society of Dyers and Colourists* 89 (1973), pp. 287–291.

[6] Stephen Brunauer, Paul Hugh Emmett and Edward Teller. 'Adsorption of gases in multimolecular layers'. In: *Journal of the American Chemical Society* 60 (1938), pp. 309–319.

[7] Matthias Thommes et al. 'Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)'. In: *Pure and Applied Chemistry* 87 (2015), pp. 1051–1069.

[8] D C Jones. 'Some comments on the BET (Brunauer–Emmett–Teller) adsorption equation'. In: *Journal of the Chemical Society* (1951), pp. 126–130.

[9] E A Guggenheim. *Applications of statistical mechanics*. Oxford: Clarendon Press, 1966.

[10] J H de Boer. *The dynamical character of adsorption*. Oxford: Clarendon Press, 1953.

[11] R H Fowler. 'A statistical derivation of Langmuir's adsorption isotherm'. In: *Mathematical Proceedings of the Cambridge Philosophical Society* (1935), pp. 260–264.

[12] R H Fowler and E A Guggenheim. *Statistical thermodynamics*. Cambridge University Press, 1939.

[13] Victor Ya Frenkel. 'Yakov Ilich Frenkel: Sketches toward a civic portrait'. In: *Historical Studies in the Physical and Biological Sciences* 27 (1997), pp. 197–236.

[14] Y I Frenkel. *Kinetic theory of liquids*. Oxford: Clarendon Press, 1946.

[15] George Halsey. 'Physical adsorption on non-uniform surfaces'. In: *The Journal of Chemical Physics* 16 (1948), pp. 931–937.

[16] Terrell L Hill. 'Physical adsorption and the free volume model for liquids'. In: *Journal of Chemical Physics* 17 (1949), pp. 590–590.

[17] Terrell L Hill. 'Theory of physical adsorption'. In: *Advances in Catalysis* 4 (1952), pp. 211–258.

[18] Robert B Anderson. 'Modifications of the Brunauer, Emmett and Teller equation'. In: *Journal of the American Chemical Society* 68 (1946), pp. 686–691.

[19] C van den Berg. 'Vapour sorption equilibria and other starch-water interactions; A physico-chemical approach'. PhD thesis. Agricultural University, Wageningen: Department of Food Science, 1981.

[20] Stephen Brunauer, Jan Skalny and E E Bodor. 'Adsorption on nonporous solids'. In: *Journal of Colloid and Interface Science* 30 (1969), pp. 546–552.

[21] T. C. Powers and T. L. Brownyard. 'Studies of the physical properties of hardened cement paste.' In: *Journal of the American Concrete Institute, Proceedings* 43 (1947), pp. 101–992.

[22] Annanias Tveit. *Measurements of moisture sorption and moisture permeability, of porous paterials*. Report 45. Oslo: Norwegian Building Research Institute, 1966.

[23] Kurt Kielsgaard Hansen. *Sorption isotherms: a catalogue*. Technical Report 162. Lyngby: Building Materials Laboratory, Department of Civil Engineering, Technical University of Denmark, 1986.

[24] M K Kumaran. *Heat, Air and Moisture Transfer Through New and Retrofitted Insulated Envelope Parts, Final report, IEA-Annex 24, Task 3: Material Properties*. 1996.

[25] Robert Černý and Pavla Rovnaníková. *Transport processes in concrete*. London: Spon Press, 2002.

[26] H M Künzel. *Simultaneous heat and moisture transport in building components: One- and two-dimensional calculation using simple parameters*. Stuttgart: Fraunhofer IRB Verlag, 1995.

[27] Aditya Kumar et al. 'Water vapor sorption in cementitious materials – measurement, modeling and interpretation'. In: *Transport in porous media* 103 (2014), pp. 69–98.

[28] Qiang Zeng, Dongdong Zhang and Kefei Li. 'Kinetics and equilibrium isotherms of water vapor adsorption/desorption in cement-based porous materials'. In: *Transport in Porous Media* 109 (2015), pp. 469–493.

[29] Martin Z Bazant and Zdeněk P Bažant. 'Theory of sorption hysteresis in nanoporous solids: Part II Molecular condensation'. In: *Journal of the Mechanics and Physics of Solids* 60 (2012), pp. 1660–1675.

[30] James M de Burgh, Stephen J Foster and Hamid R Valipour. 'Prediction of water vapour sorption isotherms and microstructure of hardened Portland cement pastes'. In: *Cement and Concrete Research* 81 (2016), pp. 134–150.

[31] Zbyšek Pavlík et al. 'Water vapor adsorption in porous building materials: experimental measurement and theoretical analysis'. In: *Transport in Porous Media* 91 (2012), pp. 939–954.

I thank Professor Ole Jensen for several helpful comments.

Christopher Hall
v3 (minor edits)
12 October 2025

To cite this NQ: C Hall, Isothermal history, *Hall's Notes and Queries* NQ12

Comments to: `christopher.hall@ed.ac.uk`