

**Supporting Information for:**

**Langmuir's Theory of Adsorption: a Centennial Review**

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## S1. Nomenclature

**Table S1.** Nomenclature used in this work compared to that used in *Langmuir 1918*.

Symbol	Quantity	Typical Units	Langmuir's Symbol <sup>3</sup>
$r$	surface rate	$\text{m}^{-2} \text{s}^{-1}$	$\nu, \mu$
$p$	probability	(dimensionless)	$\alpha$
$\theta$	fractional site occupancy	(dimensionless)	$\theta_i$
--	relative adsorption lifetime	$\text{m}^2 \text{s}$	$\sigma$
$N$	number	(dimensionless)	$N$
$n$	mole number	mol	$\eta$
$T$	temperature	K	$T$
$P$	pressure	Pa	$p$
$V$	volume	$\text{m}^3$	$V$
$m$	molecular mass	kg	$M$
$R$	gas constant	$\text{J K}^{-1} \text{mol}^{-1}$	$R$
$K$	Langmuir binding constant	$\text{Pa}^{-1}$	$a_i$
$\Gamma$	Langmuir scaling constant	$\text{mmol g}^{-1}$	$b_i$
$A$	exponential prefactor	varies	--
$\alpha$	weighting constant	(dimensionless)	$\beta_i$
$n$	Hill interaction constant	(dimensionless)	--
$B$	BET variable	$\text{g mmol}^{-1}$	--
$c$	BET constant	(dimensionless)	--
$N_a$	number adsorbed	(dimensionless)	
$\Gamma$	Langmuir scaling constant	$\text{g}^{-1}$	
$U$	adsorption site binding energy	J	
$\mu$	chemical potential	J	
$q, \xi$	single-site partition function	(dimensionless)	
$Q, \Xi$	total partition function	(dimensionless)	
$\Lambda$	thermal de Broglie wavelength	m	
$\pi$	spreading pressure	$\text{N m}^{-1}$	

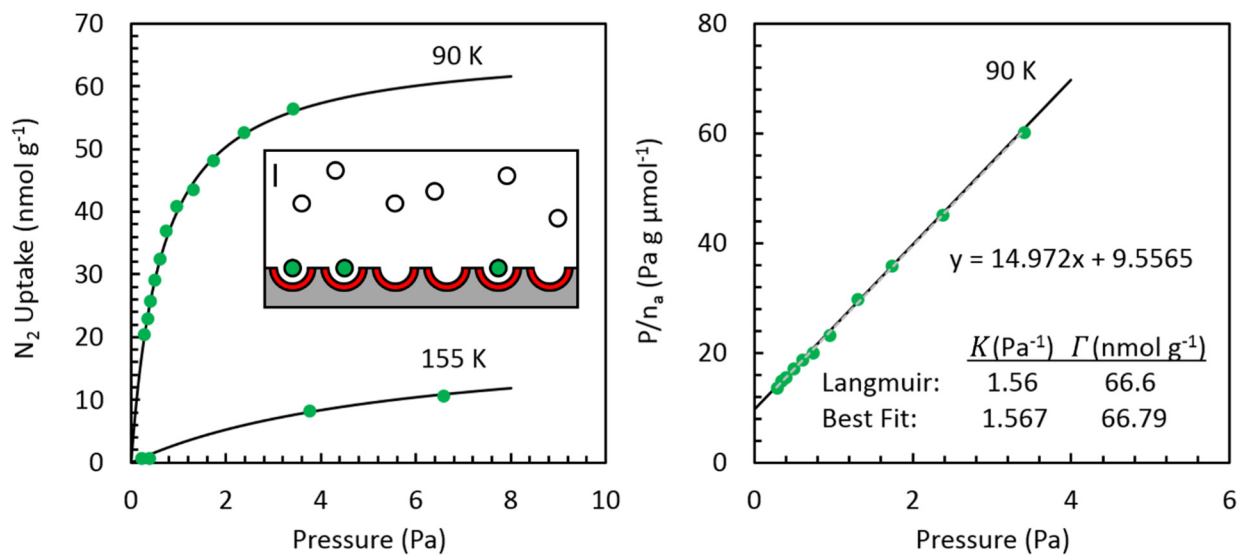
## S2. Langmuir 1918: Experimental Notes

### Data Analysis

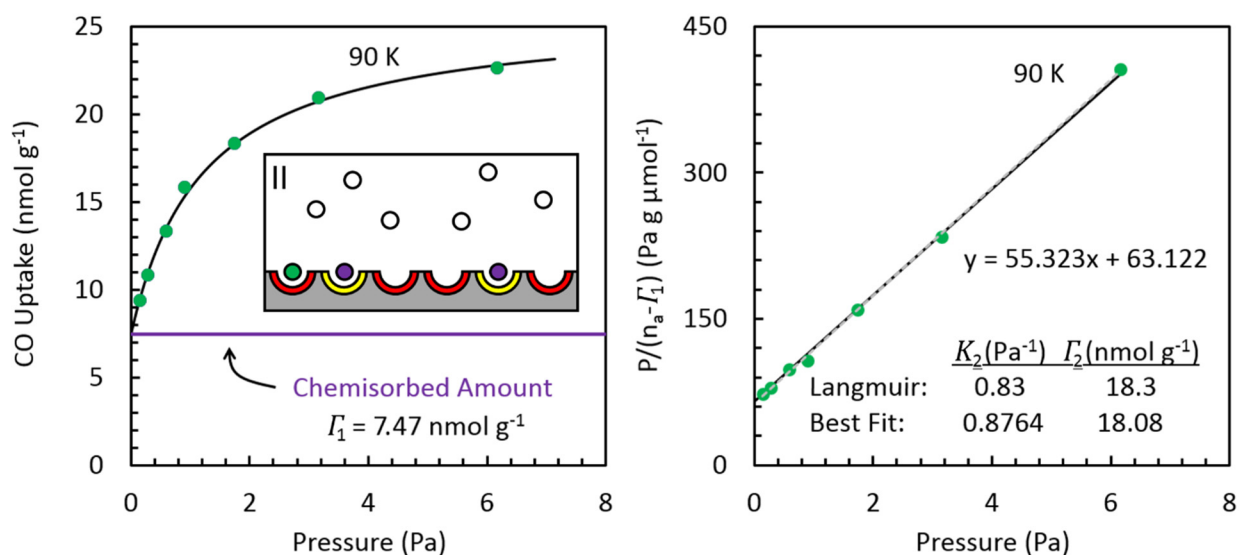
Langmuir reported in 1918 that the experimental desorption equilibria were fitted “by a somewhat laborious method of trial” (and, presumably, error).<sup>3</sup> A selection of the originally reported data are plotted and fitted in **Figure S1** and **Figure S2**. Upon modern inspection of the data, it is apparent that Langmuir did not use a purely unbiased approach to the fitting procedure. For example, in evaluating N<sub>2</sub> desorption on mica at 155 K, Langmuir chose to exclude one of the four data points as an outlier, fitting only three points to find the Langmuir constants (**Figure S3**). Similarly, in assessing the goodness of fit of the DSL model to CO desorption on glass, Langmuir exploited *a priori* chemical knowledge of the system and experimental observation of a certain “non-desorbing quantity” ( $\Gamma_1 = 7.47 \text{ nmol g}^{-1}$ ) to justify ignoring the use of a simpler **SSL** model despite the lack of a purely statistical justification (the data are actually fitted well by an **SSL** equation). These facts are testament to the ever-present role of chemical insight in the analysis and interpretation of experimental adsorption equilibria.

### Units

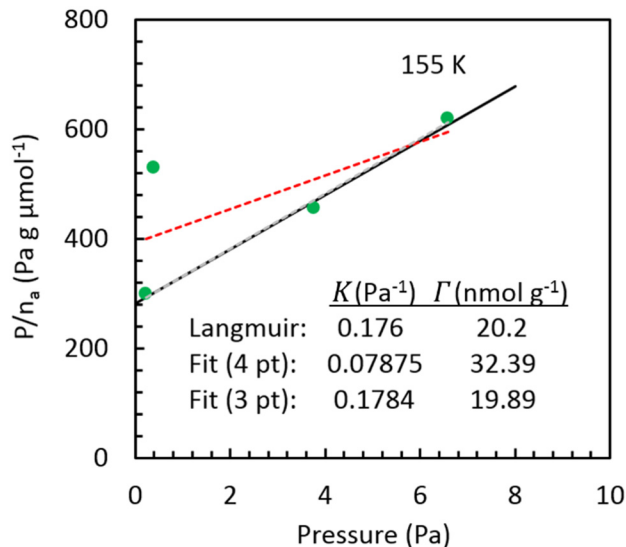
It is interesting to note that the desorption equilibria reported by Langmuir in 1918 are tabulated as a function of pressure in units of “bars,” which we have deduced to be an antiquated use of the nomenclature before standardization of the units now referred to as “bar” (accepted to indicate 1 megadyne per square centimeter) and “barye” or “barad” (accepted to indicate 1 dyne per square centimeter). Hence, Langmuir was actually measuring and reporting in units of microbar or decipascal (in modern nomenclature). This confusion of pressure units nomenclature was addressed by Charles Marvin in 1918<sup>4</sup> and Alexander McAdie specifically referred to Langmuir’s work in his (unsuccessful) attempt to revive the initial (more “physical”) definition of the unit “bar” in 1922<sup>5</sup>. The meteorological convention (where 1 bar  $\approx$  1 atm) eventually prevailed, and remains in use today. Bror Gustaver also confirms that Langmuir made his original measurements at remarkably low pressures, only up to “100 bars = 0.1 mm Hg.”<sup>6</sup> The quantity adsorbed was measured along the desorption branch only and reported in units of standard cubic millimeters (left as unnormalized with respect to sample mass). Since the mass of each sample was also reported, we have converted these values to standard cubic centimeters (mL<sub>STP</sub>) per gram as well as units such as mmol g<sup>-1</sup>,  $\mu\text{mol g}^{-1}$ , and nmol g<sup>-1</sup> for the purposes of the analysis in this review.



**Figure S1.** Equilibrium desorption measurements of  $\text{N}_2$  on mica at 90 and 155 K as reported in *Langmuir 1918* (left) and the corresponding Langmuir plot (right), showing the originally reported fit (solid black line) and the best fit using modern linear regression analysis (dashed gray line).



**Figure S2.** Equilibrium desorption measurements of  $\text{CO}$  on glass at 90 K as reported in *Langmuir 1918* (left) and the corresponding modified Langmuir plot (right), showing the originally reported DSL fit (solid black line) and the best DSL fit using modern linear regression analysis (dashed gray line). The strongly bound quantity originally reported (attributed to chemisorption) is also shown (solid purple line).



**Figure S3.** Langmuir plot of  $\text{N}_2$  desorption on mica at 155 K showing the originally reported fit (solid black line) and two fits using modern linear regression analysis: a fit to all four data points (dashed red line) and a fit to three of the four data points, chosen to reproduce Langmuir’s result (dashed gray line).

### S3. Kinetic Derivation of Langmuir’s Theory

Langmuir described gas adsorption at a solid interface as bearing mechanistic similarity to gas-phase condensation at a liquid surface, where inelastic collisions lead to a “lag” or residence time at the location of incidence.<sup>1</sup> That is, as gas molecules strike the surface, they are held near the surface by attractive intermolecular forces (akin to condensation) for some short but finite time until leaving into the bulk gas phase again (akin to evaporation). Within this kinetic view of adsorption, and with his newly devised concept of the discretized, surface-oriented nature of adsorption in hand, Langmuir derived a simple relationship between equilibrium site occupancy,  $\theta$ , and the pressure of the gas phase,  $P$ .

Langmuir made three fundamental assumptions:

- (i) the rate of incidence of the molecules in a bulk gas phase on a unit area of adsorbent surface,  $r_{inc}$ , is proportional to the pressure at constant temperature via the kinetic theory of gases (adapted from his previous work on saturated metal vapors above their respective solids<sup>7</sup>),
- (ii) the rate of adsorption (as opposed to metal vapor condensation),  $r_{ads}$ , depends not only on the rate of incidence of molecules on the surface,  $r_{inc}$ , but also on the probability of adsorption (as opposed to elastic reflection),  $p_{ads}$ , and the probability of incidence at a *vacant* adsorption site (as opposed to at an occupied site),  $p_{vac}$ , and

- (iii) the rate of desorption is equal to the rate of desorption at maximum surface coverage,  $r_{des,sat}$ , multiplied by the fractional occupancy of the surface sites by adsorbed molecules,  $\theta$  (thereby neglecting any role of adsorbate-adsorbate interactions).

Mathematically, for an adsorptive of molar mass  $m$ , these observations can be summarized as:

$$r_{inc} = \frac{P}{\sqrt{2\pi mRT}} \propto P \quad \text{Equation S1}$$

$$r_{ads} = r_{inc} \cdot p_{ads} \cdot p_{vac} \quad \text{Equation S2}$$

$$r_{des} = r_{des,sat} \cdot \theta \quad \text{Equation S3}$$

These “surface rates” have dimensions of inverse time, per unit area. The probability of incidence at a vacant site is equal to the fraction of unoccupied sites on the surface, or the difference between 1 and the fraction of occupied sites,  $(1 - \theta)$ , giving:

$$r_{ads} = r_{inc} \cdot p_{ads} \cdot (1 - \theta) \quad \text{Equation S4}$$

Then owing to the simple requirement that the flux of molecules onto and off of the surface must be equal at equilibrium, the fractional occupancy of the surface is found as:

$$r_{ads} = r_{des} \quad \text{Equation S5}$$

$$r_{inc} \cdot p_{ads} \cdot (1 - \theta) = r_{des,sat} \cdot \theta \quad \text{Equation S6}$$

$$\theta = \frac{r_{inc} \cdot p_{ads}}{r_{des,sat} + r_{inc} \cdot p_{ads}} = \frac{KP}{1 + KP} \quad \text{Equation S7}$$

The Langmuir constant,  $K$ , is thus defined as:

$$K = \frac{1}{\sqrt{2\pi mRT}} \cdot \frac{p_{ads}}{r_{des,sat}} \quad \text{Equation S8}$$

## S4. Statistical Mechanical Derivations of Langmuir's Theory

Six adsorption classifications were presented by Langmuir in 1918:

**Case I** is “simple” or single-site Langmuir (**SSL**) adsorption; all adsorption sites are equivalent.

**Case II** is multi-site Langmuir (**MSL**) adsorption and is especially useful, for example, in systems involving both chemisorption and physisorption sites.

**Case III** is generalized Langmuir (**GL**) adsorption where a diversity of binding sites is present on the surface (as on an amorphous solid).

**Case IV** is cooperative Langmuir adsorption (**CA**), for single-site adsorption of multiple molecules per site, where cooperative interactions are permitted between molecules adsorbed on the same site.

**Case V** is dissociative Langmuir adsorption (**DA**), where the number of adsorption sites occupied is an integer multiple of the number of adsorbed molecules, a chemisorption process.

**Case VI** is multilayer Langmuir adsorption (**MLA**); each simple adsorption site can accommodate multiple occupants with differing binding energies.

There are four special cases of the above six general classifications, indicated by an asterisk:

**Case II\*** is dual-site Langmuir (**DSL**) adsorption and is especially useful, for example, in systems having distinct chemisorption and physisorption sites.

**Case III\*** is “Unilan” or uniform Langmuir (**UL**) adsorption and is a special case of multi-site adsorption where all of the binding site energies are unique and uniformly distributed between a minimum and maximum.

**Case IV\*** is quadratic adsorption (**QA**), for single-site adsorption of up to two molecules per site (with cooperative interactions when doubly occupied).

**Case VI\*** is Brunauer-Emmett-Teller (**BET**) adsorption and is a special case of multilayer adsorption where the first layer is distinguished from all higher layers by a different binding energy.

In each derivation, we consider a surface (covering a unit gram of adsorbent material) composed of  $\Gamma$  elementary adsorption sites, each capable of hosting one or more adsorbed molecules. In all cases, the bulk fluid phase above the adsorbed phase is taken to be ideal. The volume of a given binding site is  $V_{B,i} = |\Omega_{B,i}|$ , where  $\Omega_{B,i}$  is the set of points comprising the adsorption site, and the binding energy of a given site of type  $i$  is  $U_i$ . The single-site grand canonical partition function,  $\xi$ , and the total grand canonical partition function,  $\mathcal{E}$ , for each case are shown in **Table S2**.

**Table S2.** Grand canonical partition functions and adsorption isotherm for each of Langmuir's six cases identified in *Langmuir 1918*.

	Common Name	Partition Function	Adsorption Isotherm Equation
Case I	Single-Site (SSL)	$\xi(\mu, V, T) = 1 + \Lambda^{-3} V_B e^{-\beta U_1} e^{\beta \mu}$ $\Xi(\mu, V, T) = \xi^\Gamma$	$N_a(P) = \Gamma \frac{K_1 P}{1 + K_1 P}$
Case II	Multi-Site (MSL)	$\xi_i(\mu, V, T) = 1 + \Lambda^{-3} V_{B,i} e^{-\beta U_i} e^{\beta \mu}$ $\Xi(\mu, V, T) = \prod_{i=1}^{\text{types}} \xi_i^{\Gamma_i}$	$N_a(P) = \sum_{i=1}^{\text{types}} \Gamma_i \frac{K_i P}{1 + K_i P}$
Case II*	Dual-Site (DSL)	$\xi_i(\mu, V, T) = 1 + \Lambda^{-3} V_{B,i} e^{-\beta U_i} e^{\beta \mu}$ $\Xi(\mu, V, T) = \xi_1^{\Gamma_1} \xi_2^{\Gamma_2}$	$N_a(P) = \Gamma_1 \frac{K_1 P}{1 + K_1 P} + \Gamma_2 \frac{K_2 P}{1 + K_2 P}$
Case III	Generalized Langmuir (GL)	$\xi_i(\mu, V, T) = 1 + \Lambda^{-3} V_{B,i} e^{-\beta U_i} e^{\beta \mu}$ $\Xi(\mu, V, T) = \prod_{i=1}^{\Gamma} \xi_i$	$N_a(P) = \sum_{i=1}^{\Gamma} \frac{K_i P}{1 + K_i P}$
Case III*	Unilan (UL)	Same as for <b>GL</b> , but uniform distribution: $U_{min} \leq U_i \leq U_{max}$	$N_a(P) = \frac{\Gamma}{2s} \ln \left( \frac{1 + K_{avg} e^s P}{1 + K_{avg} e^{-s} P} \right)$
Case IV*	Quadratic (QA)	$\xi(\mu, V, T) = 1 + 2\Lambda^{-3} V_B e^{-\beta U_1} e^{\beta \mu} + \Lambda^{-6} V_B^2 e^{-\beta(2U_1 + U_{AA})} e^{2\beta \mu}$	$N_a(P) = \Gamma \frac{2KP + 2K^2 \phi P^2}{1 + 2KP + K^2 \phi P^2}$
Case V	Dissociative (DA)	$\xi(\mu, V, T) = 1 + \Lambda_A^{-3} V_B e^{-\beta U_1} e^{\beta \mu_A}$	$N_a(P) = \Gamma \frac{K\sqrt{P}}{1 + K\sqrt{P}}$
Case VI*	Brunauer, Emmett, and Teller ( <b>BET</b> )	$\xi(\mu, V, T) = 1 + \frac{q_1 e^{\beta \mu}}{1 - q_l e^{\beta \mu}}$ $\Xi(\mu, V, T) = \xi^\Gamma$	$N_a(P) = \Gamma \frac{KP}{(1 - K_l P)(1 + (K - K_l)P)}$

Note: in the sums and products in **Table S2**,  $i$  indicates a specific type of adsorption site (indexed from 1 up to the number of different types of site).



## References

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