Exercise 1 Langmuir isotherm

Consider an experiment to study the adsorption of hydrocarbons onto silica gel. The amount of butane adsorbed onto the gel surface is measured at various pressures of gas at 303 K and summarized in the following table.

P (bar)	0.1	0.2	0.3	0.4	0.5
n (mmol)	0.36	0.68	0.98	1.24	1.49

(a) What is the coverage θ?

(b) Demonstrate that the adsorption follows a Langmuir isotherm. *Hints: write a linear relation between* $1/n$ *as a function of* $1/P$.

(c) Determine the total number of adsorption sites.

(d) Determine the Langmuir adsorption constant k.

(e) Assuming $\theta = 1$, how many butane molecules do you need to cover fully the available surface? *Hints: the Avogadro number* N_A *is* $6.022 \times 10^{23}\,\mathrm{mol}^{-1}$.

(f) Maintaining the temperature constant at $T = 303K$, determine the pressure of gas required to achieve a surface coverage of 30%?

(g) Start from a fully covered surface and allow the butane to desorb by decreasing the pressure to that corresponding to coverage $\theta = 0.5$. What is the volume of the gas produced?

Solution to Exercise 1

(a) During an adsorption experiment, the coverage θ can be defined as

$$\theta = \frac{\text{Number of surface sites occupied by adsorbate } (N_s)}{\text{Total number of substrate adsorption sites } (N)} = \frac{n}{n_\infty}.$$

(b) The dependence of θ in the gas pressure P is the adsorption isotherm. The expression for the Langmuir adsorption as a function of the gas pressure is

$$\theta = \frac{kP}{1 + kP}.$$

Expressing θ in terms of the amount of gas adsorbed relative to the amount that corresponds to complete monolayer coverage and inverting the equation, the Langmuir isotherm can be recast in the following form:

$$\frac{1}{\theta} = \frac{n_\infty}{n} = \frac{1}{kP} + 1 \longrightarrow \frac{1}{n} = \frac{1}{n_\infty k}\frac{1}{P} + \frac{1}{n_\infty}.$$

(c) If the Langmuir isotherm is obeyed, plotting $1/n$ versus $1/P$ should result in a straight line with intercept on the y–axis $1/n_\infty$. In our case $1/0.147 = n_\infty = 6.803\,\text{mmol}$.

(d) The linearized version of the Lagmuir equations as gradient $1/n_\infty k = 0.263$, so $k = 0.559\,\text{bar}^{-1}$.

(e) Knowing n_∞, the number of molecules is

$$n_\infty N_A = 6.803 \times 10^{-3}\,\text{mol} \times 6.022 \times 10^{23}\,\text{mol}^{-1} = 4.097 \times 10^{21}$$

(f) We may rearrange

$$\theta = \frac{kP}{1+kP}$$

in order to determine the pressure required for a given surface coverage:

$$P = \frac{\theta}{(1-\theta)k} = \frac{0.3}{(1-0.3)0.559} = 0.767\,\text{bar}.$$

(g) We have first to compute the pressure corresponding 50% of surface coverage.

$$P = \frac{\theta}{(1-\theta)k} = \frac{0.5}{(1-0.5)0.559} = 1.789 \times 10^5\,\text{Pa}.$$

A coverage of 0.5 means that $n = n_\infty/2$, so $n = 3.401\,\text{mmol}$.

We then calculate the amount of gas desorbed from the surface of the silica gel using the perfect gas equation, remembering that $\text{Pa} = \text{J}\,\text{m}^{-3}$

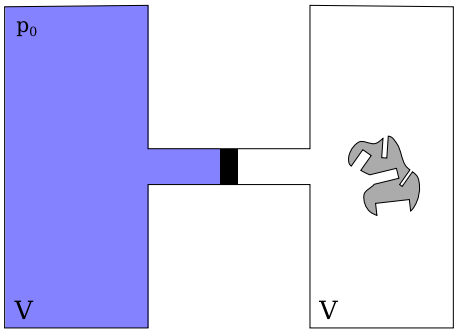
$$PV = nRT \longrightarrow\ V = \frac{3.401 \times 10^{-3}\,\text{mol} \times 8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} \times 3.03 \times 10^2\,\text{K}}{1.789 \times 10^5\,\text{Pa}} = 47.89\,\text{cm}^3$$

Exercise 2 Langmuir adsorption and surface areas

We want to measure the surface area A_2 of a porous material. Assume we have a compact sample of the same material, with known surface area $A_1 = 1\,\text{cm}^2$. The experiment we perform goes as follows:

- There are two chambers separated by a valve. The volume of each chamber is $V = 1\,\text{dm}^3$, and the volume of the connecting pipes and of the sample is negligible. We also assume that no gas is adsorbed on the walls of the chambers. Everything is run at constant temperature $T = 300\,\text{K}$.
- We evacuate the chamber that contains the sample, so that all of the possibly adsorbed molecules desorb. We fill the other chamber with a known pressure $p_0 = 10^3\,\text{Pa}$ of nitrogen, that **is assumed to behave as a perfect gas**.
- We open the valve and let the system equilibrate. We measure the overall pressure. We repeat the experiment with the reference sample of known area, obtaining the final pressure $p_1 = 4 \times 10^2\,\text{Pa}$, and with the sample of unknown area, obtaining the final pressure $p_2 = 2 \times 10^2\,\text{Pa}$.

Cont.



(a) How many moles of N_2 are present in the gas phase before the valve is open, and for the two samples after equilibration? Obtain as a difference the number of moles that have been adsorbed by the two samples.

(b) Assuming that the adsorption of molecules on the material is described by a Langmuir isotherm,

$$\theta = \frac{n}{n_\infty} = \frac{n}{A/\sigma} = \frac{kp}{1+kp},$$

where σ is the area associated with each adsorption site, **and that we are in a regime with very low coverage with** $k\,p \ll 1$, compute the surface area of the unknown sample A_2.

Solution to Exercise 2

(1) Assuming that is valid the law of a perfect gas, $pV = nRT$, we have

$$n_0^g = p_0 V/RT$$

and inserting the numbers given in the text (the universal gas constant: $R = 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$), we obtain $n_0^g = 0.40 \times 10^{-3}\,\mathrm{mol}$.

Similarly, but considering that after opening the valve the volume has doubled

$$n_1^g = 0.32 \times 10^{-3}\,\mathrm{mol},$$

$$n_2^g = 0.16 \times 10^{-3}\,\mathrm{mol}.$$

So we obtain that the first sample has adsorbed $n_1 = 0.08 \times 10^{-3}\,\mathrm{mol}$ and the second sample $n_2 = 0.24 \times 10^{-3}\,\mathrm{mol}$.

(2) According to the Langmuir isotherm, if we are in the case $\alpha p \ll 1$ we can approximate it as

$$\frac{\sigma n}{A} \approx k\,p$$

hence

$$\sigma\frac{n_1}{A_1} = k\,p_1, \qquad \sigma\frac{n_2}{A_2} = k\,p_2$$

dividing each side and then inserting the numbers

$$\frac{A_2}{A_1} = \frac{p_1 n_2}{p_2 n_1} = 6,$$

so $A_2 = 6A_1 = 6\,\mathrm{cm}^2$.

The End.