1. 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 303K 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 θ=1, how many butane molecules do you need to fully cover the available surface?
Hints: the Avogadro number N_A is 6.022×10^{23} 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 θ = 0.5. What is the volume of the gas produced?

Solution:

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

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

(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:

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

(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 $1/0.147 = n_\infty = 6.803$ mmol.

(d) The linearized version of the Langmuir equations as gradient $1/n_\infty k = 0.263$, so $k = 0.559$ 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:

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

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

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

A coverage of 0.5 means that n = n∞/2, so n = 3.401 mmol.

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

$$PV = nRT \rightarrow V = \frac{3.401\times10^{-3} mol \times 8.3145 J/K\cdot mol \times 3.03\times10^2 K}{1.789\times10^5 Pa} = 47.89 cm^3$$

2. The Gibbs adsorption isotherm relates the changes in surface tension of a mixture to the change in the chemical potential (or concentration) of a solute:

$$d\gamma = -RT\frac{\Gamma}{c}dc$$

Consider the concentration dependence of the surface tension of a water/ethanol mixture at 20 °C:

$x_{ethanol}$	0.020	0.042	0.065
γ(mN/m)	56.41	48.14	42.72

a) Find out the relation between the surface excess Γ and the surface tension of the solution at two different concentrations.

b) Compute the surface excess of ethanol Γ considering the interval between 2% and 4% molar concentration.

c) Compare it with the excess computed using the interval between 4% and 6.5% molar concentration. How does the surface excess change as a function of concentration?

d) Is the concentration of ethanol in the vicinity of the surface larger or smaller than in the bulk of the solution?

Solution:

(a) Integrate the first equation over a finite concentration change and get

$$\int_{\gamma_1}^{\gamma_2} d\gamma' = -RT\Gamma \int_{c_1}^{c_2} \frac{dc'}{c'} \quad \rightarrow \quad \gamma_2 - \gamma_1 = -RT\Gamma \ln \quad \frac{c_2}{c_1}$$

The surface excess is then

$$\Gamma = \frac{\gamma_2 - \gamma_1}{RT ln\ \frac{c_1}{c_2}}$$

(b) We can obtain Γ from

$$\Gamma = \frac{\gamma_2 - \gamma_1}{RT\ ln\ ln\ \frac{c_1}{c_2}} = \frac{(48.14 - 56.41)x10^{-3} N/m}{8.31 J/K \cdot mol \times 293 K x ln\ \frac{0.02}{0.042}} = 3.395 \times 10^{-6} mol/m^2$$

(c) Repeating for the second interval,

$$\Gamma = 5.09 \times 10^{-6} mol/m^2$$

Considering the experimental uncertainty, the Gibbs isotherm holds very well.

(d) The surface excess Γ describes the excess of solute relative to the solvent. Since it is positive, there is a larger concentration of ethanol at the surface than in the bulk. Note that we could have seen this just by looking at the fact that γ was decreasing with increasing concentration of ethanol.