16. ADSORPTION

$$\Gamma_{2,1} = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln c_2}\right)_{T,p} = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_{T,p} \qquad ; \qquad \Gamma_{2,1} = \frac{1}{\mathcal{A}}\left(n_2^s - \frac{n_2}{n_1}n_1^s\right)$$

$$a = k \cdot p^{1/n}$$

$$a = a_m \frac{b \cdot p}{1 + b \cdot p} \quad , \quad \frac{p}{a} = \frac{1}{b \cdot a_m} + \frac{p}{a_m} \quad , \qquad \mathcal{A}_{sp} = a_m \cdot \sigma \cdot N_A$$

$$\left(\frac{\partial \ln p}{\partial T}\right)_a = -\frac{Q_{dif}(a)}{RT^2}$$

$$\Omega_2 = \frac{V^o}{m_s}\cdot(c_2^0 - c_2)$$

$$\Omega_2 = k\cdot c_2{}^n$$

$$\Omega_2 = \Omega_m \frac{b \cdot c_2}{1 + b \cdot c_2} \quad , \quad \frac{c_2}{\Omega_2} = \frac{1}{b \cdot \Omega_m} + \frac{c_2}{\Omega_m} \quad , \qquad \mathcal{A}_{sp} = \Omega_m \cdot \sigma \cdot N_A$$

Adsorption on the interface solution – gaseous phase

Problem 16-01 Gibbs adsorption isotherm

The concentration dependence of the surface tension of diluted solutions of a surfactant at the temperature of 25 °C was expressed by the following equation:

$$\gamma = 7.2\cdot 10^{-2} - 6.445\cdot 10^{-3}\cdot c_2 + 1.14\cdot 10^{-3}\cdot c_2{}^2$$

c_2 is the concentration of the solute (mol dm^{-3}) and γ surface tension (N m^{-1}). Find an equation describing the concentration dependence of the relative Gibbs adsorption, $\Gamma_{2,1}$.

$$[\Gamma_{2,1} = 2.6\cdot 10^{-6}\cdot c_2 - 9.2\cdot 10^{-7}\cdot c_2{}^2]$$

Problem 16-02 Gibbs adsorption isotherm

The surface tension of the diluted aqueous hexanol solutions at the temperature of 26.5 °C can be expressed as a linear function of alcohol concentration in the bulk phase

$$\gamma = 0.0716 - 6.8\cdot c_2$$

where γ is the surface tension (N m^{-1}) and c_2 is the concentration in mol dm^{-3}. Calculate the relative adsorption with respect to water as a solvent, $\Gamma_{2,1}$, in a solution of concentration $6\cdot 10^{-4}$ mol dm^{-3}. Is it possible to say that hexanol is a surface active substance?

$$[\Gamma_{2,1} = 1.637\cdot 10^{-6}\ \text{mol m}^{-2} > 0 \text{ - hexanol is a surface active substance }]$$

Adsorption of gases on solid surfaces

Problem 16-03 Langmuir adsorption isotherm

The adsorption of methane on the solid adsorbent can be described by Langmuir adsorption isotherm. The surface area of 3.4 g of the solid adsorbent is 629 m^2. One adsorbed methane molecule occupies on the solid surface an area $\sigma = 0.25$ nm^2. One of experiments revealed that at equilibrium pressure 62.9 kPa the capacity of the solid surface for methane adsorption was saturated from 65 %. Determine the constants of Langmuir isotherm. ($M_{CH4} = 16.043$ g mol^{-1}).

$$[a_m = 0.00123\ \text{mol}_{CH4}/\text{g}_s = 0.0197\ \text{g}_{CH4}/\text{g}_s\ ;\ b = 0.03\ \text{kPa}^{-1}]$$

Problem 16-04 Gas adsorption on solids, Langmuir adsorption isotherm, specific area

Experimental data on adsorption of pentane on the charcoal at the temperature of 230 °C were well described by the Langmuir isotherm

$$v = \frac{1.953 \cdot p}{1 + 0.09 \cdot p}$$

v denotes the volume of the gas (cm^3, corrected to standard conditions 273.15 K and 101.325 kPa), adsorbed on 1 g of charcoal, and p equilibrium pressure (kPa). Calculate the total area of 5 g of charcoal. One molecule of pentane occupies on the surface of the charcoal an area of 0.76 nm^2.

$[A = 2215.6 \text{ m}^2 \ (v_m = 21.7 \text{ cm}^3 \text{ g}^{-1})]$

Problem 16-05 Gas adsorption on solids – Langmuir adsorption isotherm

The specific area of a solid adsorbent is 230 m^2 g^{-1}. Experiments revealed that 18 cm^3 of argon (corrected to standard conditions) is adsorbed on 1 g of this adsorbent at equilibrium pressure of 22 kPa. Assuming that adsorption in this system is adequately described by the Langmuir isotherm, calculate the volume of argon adsorbed on the surface of 26 g of the solid at equilibrium pressure of 90 kPa. One atom of argon occupies on adsorption on the solid surface the area of 0.2 nm^2.

$[V = 832.5 \text{ cm}^3 \text{ on 26 g } \ (v_m = 42.8 \text{ cm}^3 \text{ g}^{-1}, \ b = 0.033 \text{ kPa}^{-1}, \ v_2 = 32.02 \text{ cm}^3 \text{ g}^{-1})]$

Problem 16-06 Gas adsorption on solids – Freundlich isotherm

The adsorption of certain gas on silica which was studied at constant temperature of 52 °C, is well described by Freundlich equation. Using the following results of two experiments

Equilibrium pressure	Adsorbed amount
$p_1 = 27.5$ kPa	$a_1 = 3.1 \cdot 10^{-3}$ mol/g$_{silica}$
$p_2 = 52$ kPa	$a_2 = 3.76 \cdot 10^{-3}$ mol/g$_{silica}$

calculate what amount of the studied gas (in grams) will be adsorbed on 56 g of silica at equilibrium pressure of 37 kPa.

$[\Delta m = 16.34 \text{ g on 56 g silica } (1/n = 0.303, \ k = 1.136 \cdot 10^{-3}, \ a_3 = 3.3916 \cdot 10^{-3} \text{ g/g}_{silica})]$

Problem 16-07 Gas adsorption on solids – Differential (isosteric) adsorption enthalpy

Adsorption of the gaseous pentane on a solid adsorbent was studied at several temperatures, always at the same adsorbed amount. At the temperature of 45.6 °C and equilibrium pressure of 39 Pa was found that 2.64 g of the gaseous hydrocarbon was adsorbed on 11 g of the solid adsorbent. At the temperature of 86 °C the same surface occupancy was achieved at equilibrium pressure of 0.16 kPa. Calculate
(a) differential adsorption enthalpy at this surface occupancy,
(b) equilibrium pressure corresponding to this surface occupancy at the temperature of 118 °C

$[Q_{dif}(a) = -33.256 \text{ kJ mol}^{-1}, \ p = 398 \text{ Pa}]$

Adsorption from solutions on solid surfaces

Problem 16-08 Adsorption from solution on solids – Freundlich isotherm

The dependence of the adsorbed amount of an organic substance (subscript $_2$) on the charcoal from aqueous solution (water is not adsorbed) at constant temperature of 29 °C is expressed by Freundlich isotherm in the form

$$\Omega_2 /(\text{mol g}^{-1}) = 2.52 \cdot 10^{-3} \cdot c_2^{0.4}$$

where c_2 is the concentration of the organics in equilibrium bulk solution (mol dm^{-3}). How much of charcoal (in grams) should be added to 350 cm^3 of aqueous solution of concentration 0.45 mol dm^{-3}, to reduce its concentration to one third of initial value?

$$[m_s = 89 \text{ g}]$$

Problem 16-09 Adsorption from solution on solids – Freundlich isotherm

The following table gives the values of the preferential adsorption (Ω_2) and respective equilibrium concentrations of the bulk solution (c_2) obtained during the measurement of adsorption of acetic acid (subscript $_2$) from an aqueous solution on the charcoal:

c_2 / (mol dm^{-3})	Ω_2 / (mol g$^{-1}_{\text{charcoal}}$)
0.0181	$4.660 \cdot 10^{-4}$
0.8827	$2.479 \cdot 10^{-3}$

If you know that water is not adsorbed on the charcoal and that adsorption can be described by the Freundlich isotherm, calculate
(a) both constants of Freundlich equation,
(b) mole amount of the acetic acid removed from 400 cm^3 of solution by adsorption on 50 g of charcoal, if the concentration of equilibrium bulk solution was found to be 0.3 mol dm^{-3}.

$$[\text{(a) } n = 0.432; \; k = 2.64 \cdot 10^{-3} \text{ mol (g}_{\text{charcoal}})^{-1}; \text{ (b) } n = 0.0785 \text{ mol}]$$

Problem 16-10 Adsorption from solution on solids – Langmuir isotherm

The specific area of the charcoal sample was determined by means of the adsorption from the methylene blue solution. Only methylene blue is adsorbed from the solution and the adsorption data are well expressed by Langmuir isotherm. One molecule of the methylene blue occupies in the monolayer an area of 0.62 nm^2. Calculate the specific area of the adsorbent from the results of these two experiments:

(A) the equilibrium concentration of the bulk solution found after shaking 1 g of charcoal with 100 cm^3 of the solution of concentration $1 \cdot 10^{-4}$ mol dm^{-3} was $6 \cdot 10^{-5}$ mol dm^{-3},

(B) the shaking of 2 g of charcoal with the same volume of the solution of the same concentration resulted in equilibrium concentration of the bulk solution $4 \cdot 10^{-5}$ mol dm^{-3}.

$$[\mathcal{A}_{\text{sp}} = 4.48 \text{ m}^2 \text{ g}^{-1}]$$