Block 2, Assignment 1
Deadline 26 September 2025

Classical Thermodynamics - 60 points

Langmuir is one of the simplest models to explain gas adsorption on solid surfaces and it is described by the following formula:

$$q = \frac{q_{sat} k(T) P}{1 + k(T) P}$$

Where $q(mol.kg^{-1})$ is the gas uptake at a given pressure $P(Pa)$, $q_{sat}(mol.kg^{-1})$ is the saturation loading and $k(Pa^{-1})$ is the equilibrium constant.

Furthermore, the equilibrium constant is a function of temperature and is described by the Van't Hoff equation:

$$k(T) = k_0 \exp\left(\frac{-\Delta H}{RT}\right)$$

Where, $k_0(Pa^{-1})$ is the standard equilibrium constant, $\Delta H(kJ.mol^{-1})$ is the heat of adsorption, $T(K)$ is the temperature and $R(kJ.mol^{-1}.K^{-1})$ is the ideal gas constant.

1. State the basic three assumptions of the Langmuir model (2 each)

2. Prove that:
   a. At high pressure ($P \to \infty$), the gas uptake reaches a plateau (5)
   b. At low pressure ($P \to 0$), the gas uptake is a linear function of pressure (5)

3. Deduce the temperature dependence of the Henry's coefficient (3)
   Hint: Use the answer to the previous question

A researcher is interested in determining the Langmuir parameters ($q_{sat},\ k_0\ and\ \Delta H$) for CO_2 adsorption using an organic metal framework (MOF). She used computational techniques to obtain the CO_2 adsorption isotherms at three different temperatures: 263, 303 and 343 K.

4. Explain mathematically in two steps, with the help of graphs, how she can obtain the different parameters by (1st step) fitting the isotherms to the Langmuir model, (2nd step) then using the Van't Hoff equation. Keep in mind, that q_{sat} is independent of temperature and is computed only once at 263 K (11 each)

5. Fill in the code "LangCH-315.ipynb" in order to:
   a. Compute the missing Langmuir parameters (3 each)
   b. Calculate Henry's coefficient for each temperature (3 each) and discuss the trend (4)

Statistical Thermodynamics - 40 points

In adsorption studies, the heat of adsorption at zero loading is an important property and is best calculated using the Canonical Statistical Ensemble (N, V, T).

1. In the context of adsorption, describe the Canonical Ensemble in a few words (8)
2. Write the partition function (Q) for the Canonical Ensemble (4)
3. Write the probability (P_v) of finding the system in a microstate given by E_v (4)
4. Prove that (6 each):

$$\langle S\rangle = k_B ln\text{Q} + k_B T\left(\frac{\partial ln\text{Q}}{\partial T}\right)_{N,V}$$

$$P = k_B T\left(\frac{\partial ln\text{Q}}{\partial V}\right)_{N,T}$$

$$\mu = -k_B T\left(\frac{\partial ln\text{Q}}{\partial N}\right)_{V,T}$$

$$E = k_B T^2\left(\frac{\partial ln\text{Q}}{\partial T}\right)_{V,N}$$

Hints:
Always start by the statistical definition of Entropy:

$$S = -k_B \sum P_v ln P_v$$

Always keep in mind the 1^{st} law of thermodynamics:

$$dE = TdS - PdV$$

Sometimes, it is easier to prove an equality by starting from the right hand side of the equation and converging to the left hand side.

Notes

In your notebook, use the markdown cells to describe the steps you perform and what you learned from your analysis.
Be sure to upload using the correct naming convention, where # is the letter of your group: (Group#_Block2_assignment1.zip)
For this project you should upload a single zip file (or any other archive like .tar) containing all the explanation of your code and the solution to the theoretical questions. Be sure to include **ALL** your teammate names.
Do not forget to fill in the questionnaire of contribution. (If NOT filled, we assume equal contribution).