Homework 2 Advanced Materials Thermodynamics
Due September 9, 2024

Membrane separation of gasses is classically seen as a two-stage process involving a) the solubility of the gas in the membrane and b) the permeability of the gas through the membrane, the later governed by a thermally activated process following the Arrhenius function so that the transport rate increases with temperature for a given solubility. Dementyev recently investigated nanoporous carbon membranes produced by deposition of a thin carbon film and production of uniform nanopores using an ion beam [Dementyev P, Gölzhäuser A, *Anti-Arrhenius passage of gaseous molecules through nanoporous two-dimensional membranes* Phys. Chem. Chem. Phys. **26** 6949-(2024)]. Dementyev proposes a multistep membrane transport model that can be demonstrated with monodisperse porous nanopore molecularly thin membranes. The model involves 1) surface condensation of the gas, 2) Surface flow of the transporting molecule (here water, ammonina or isobutylene), 3) "effusion" into the pores, 4) "transfusion" through the pore. If step 1) dominates then the process is governed by vapor condensation equilibria. If step 4) dominates we might expect Arrhenius behavior. Dementyev found that transport decreased with increasing temperature, "*anti-Arrhenius behavior*". They show that this behavior follows the Calusius-Clapeyron equation and could therefore be modeled with a liquid/vapor condensation process.

a) Derive the Clapeyron equation and explain why it might be used to model the pressure dependence of the melting point. How is the melting point influenced by pressure?

b) Derive the Clausius-Clapeyron equation. Why is a modification of the Clausius equation needed for the vapor/liquid transition?

c) What is the normal Clausius-Clapeyron plot and how does it compare to an Arrhenius plot in the pressure-temperature space? What is obtained from the slope in the two cases? How does the Eyring Rate Theory differ from the Arrhenius Equation?

d) What is the Van't Hoff Equation. How could it be used in this study to explain the observed thermal behavior of transport through the membranes? Resketch the cartoon of Figure 4 using this Van't Hoff Model.

e) Explain Dementyev's Figures 2, 3, and 6. Why does the latent heat change with flux in Figure 5?