Workshop -3d

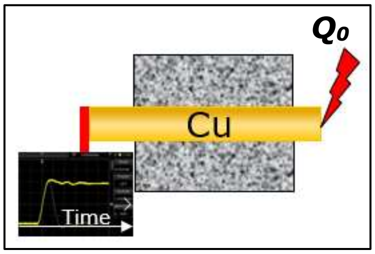
Physical Chemistry II

Exercises and Homework Set 7

Conceptional Review

- **i.** Discuss Fick's and the Fokker-Planck diffusion laws, basic relations between transport coefficients. Relation between transport of mass and transport of momentum, energy, and entropy.
- **ii.** Basic kinetics of ideal gases, applications of EoS.
- **iii.** Math of partial differentials of multi-variate functions with appropriate conditions of constant variables. Table of differentials of thermodynamic energy functions.
- **iv.** Definition of heat capacity, constant heat capacities C_v & C_p for ideal gases vs. their temperature dependence for real substances.
- **v.** Effects of particle interactions on EoS, van Der Waals model. Coexistence/spinodal curves in pV diagram of real gases. Maxwell construction.

1. Conductive Heat Transport



Heat (Q) transport in matter (specific heat capacity C) occurs both by convection and diffusive heat conduction. Conduction refers to the mean directional flux of heat time, i.e., the dependence of the average heat content $\Delta\langle Q(x,t)\rangle$ of a volume element $\Delta V = A \cdot dx$ in a rod-like sample of cross section are A. The governing equation of motion $\frac{d}{dt}\langle Q\rangle = \kappa \cdot A \cdot \frac{\partial T}{\partial x}$ depends on the conductivity coefficient $\boldsymbol{\kappa}$ and the temperature gradient in x direction. The diffusive aspect of heat conduction is governed by the rate of temperature change $\frac{\partial}{\partial t} T(x,t) = D \cdot \frac{\partial^2 T(x,t)}{\partial x^2}$, where D is the diffusion coefficient. This effect cancels on average but influences the *heat front* time profile. The example of interest for the following is a 10-cm long copper bar of ***1***cm·***1***cm cross section at room temperature, which is shock heated at one end by an electrical spark, a very brief pulse of high energy deposit E_p.

Relevant material data: C_{Cu} = 0.38 J/g·K, ρ = 8.92g/cm^3. κ = 400 W/m·K at room temperature through area A = ***1***cm^2.

a) How is the heat energy Q absorbed by material related to its eventual temperature T ?

b) Write down the differential "equation of motion" suited to model heat transport in this material sample and the indicated scenario.

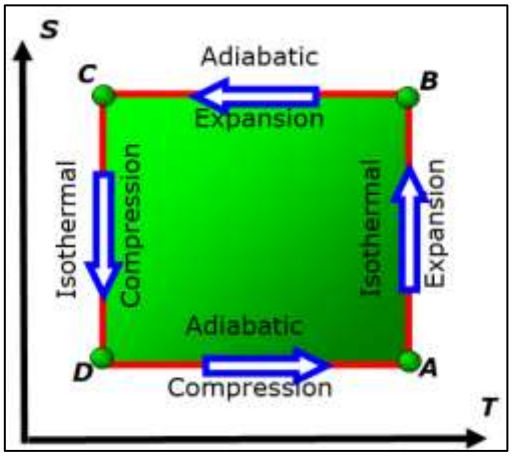
c) Identify the associated transport coefficient(s) in terms of characteristic material data for the copper sample.

d) Assume an initial energy pulse of Q(x=0, t=0) =***1***kJ. Calculate the mean arrival time t_a of of the diffuse heat front at $x = L$.

e) Calculate the steepness of the front, i.e., the rate of increase of the heat flux with time around $t = t_a$.

f) How warm will the copper bar be at long times?

2. Entropy and the Second Law of Thermodynamics



The entropy S of a system is a function of its total energy U and other variables x_i, $S=S(U, \{x_i\})$ with a differential $dS = \frac{1}{T}dU + \sum_i f_i dx_i$

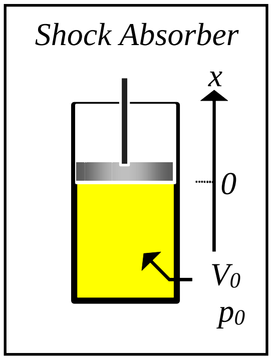
a) Show that for an ideal gas,

$$dS = \frac{C_p}{T}dT - \frac{R}{p}dp$$

b) Calculate the gain in entropy of one mole of O_2 heated from 300K to 500K under constant pressure of p =***1*** bar. For oxygen, not a perfectly ideal gas, the heat capacity depends on the temperature T as $C_p(T) = \alpha + \beta T + \gamma T^2$ with α = 25.5J/K, β = 13.6 · 10^{-3}J/K^2, and γ = -42.6 · 10^{-7}J/K^3.

c) Sketch a Carnot process in a diagram of *S* vs. *T* (see sketch). How can one illustrate in such a diagram graphically the amount of work done by the Carnot process?

3. Adiabatic Expansion and Compression



Consider a gas-filled shock absorber with an enclosed gas volume V_0 and pressure p_0 at the equilibrium position $x_0 = 0$ of the piston. After the piston (area = *A*, mass = *m*) has been displaced from this position, e.g., by a mechanical shock, it will start oscillating. Model the process in terms of adiabatic (no heat transfer) expansion and compression of an ideal gas. The adiabatic *EOS* of an ideal gas is given as $pV^{\gamma} = const$, where $\gamma = C_p/C_V$ (= *5/3* for air).

a) Derive an equation of motion for the harmonic oscillation of the piston. (Hint: $dF = A \cdot dp$ is the Hooke's restoring force resisting compression.)

b) Calculate the eigen frequency of the oscillation.

c) How will a substitution of the ideal gas by a real gas change the operation of the shock absorber?

4. Ideal and Real Gases Equations of State

a) The density of dry air at $p=1.0$ bar and $T = 300$ K is $\rho = 1.161$ kg/m^3. Assuming that it consists entirely of N_2 and O_2 and using the ideal gas EoS, determine amount of each gas in moles in a volume of $V=1m^3$ and their mole fractions x_O and x_N.

b) The density of interstellar gas clouds is about $\rho = 10^4$ $T=10K$. Calculate the pressure

p. (The lowest vacuum obtainable in the lab is about 3 orders of magnitude poorer.)

c) (i) Calculate the number ***N*** of moles of an ideal gas at ***p=1 atm*** and ***T=298 K***. Give the number in the unit ***moles per m³***.

d) The atmospheric abundance of CO_2 is currently about 450 ppmv (parts per million by volume). Assuming a pressure of ***p=1.00 atm***, estimate the amount of CO_2 in a 10.0-km thick atmospheric layer above the surface of Earth. Mean Earth radius is equal to $\boldsymbol{R_E}$**=6370 km**. (The actual amount of CO_2 in the atmosphere is about 8.0×10^{16} moles).

e) The atmospheric content of O_2 is 20.946 % by volume. Using the result in part (d), estimate the total amount of O_2 in the atmosphere.

a) Life on Earth consumes about $\boldsymbol{N_O = 0.47 \cdot 10^{16}}$ ***moles*** of O_2 per year. What percent of the O_2 in the atmosphere does life consume in a year?