ChE-403 Problem Set 1.1

Week 1

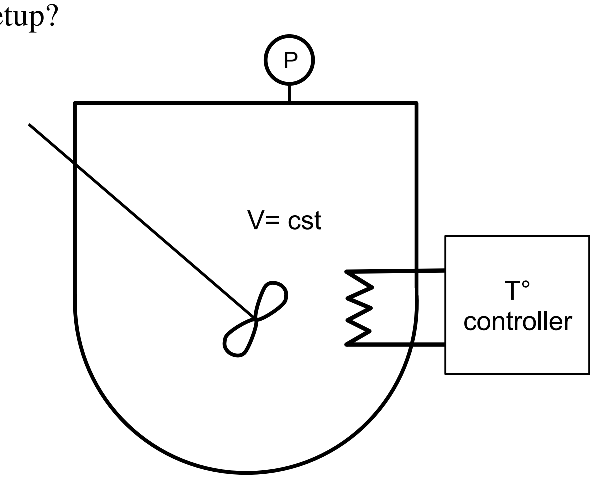
Problem 1

Take the following gas phase decomposition reaction:

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

The reaction is first order in N_2O_5 and the kinetics are not affected by pressure. You can work at low pressures (<5 bars) where the ideal gas law is valid.

Can you suggest an approach for measuring the activation energy E_a with just some chemicals and this setup?



Solution:

$$\frac{dN_{N_2O_5}}{dt} = -kC_{N_2O_5}V$$

$$\frac{dC_{N_2O_5}}{dt} = -kC_{N_2O_5}$$

Reminder, conversion is: $X_i = \frac{N_i^0 - N_i}{N_i^0} = \frac{C_i^0 - C_i}{C_i^0}$ (cst V)

$$\frac{dX}{dt} = k(1 - X)$$

$$\int_0^X \frac{dX}{1 - X} = kt$$

$$\ln(1 - X) - \ln 1 = -kt$$

$$X = 1 - \exp(-kt)$$

$P = nRT/V$

for cst V and T:

$$\frac{P}{P_0} = \frac{n}{n_0}$$

Here, if we start with 1 mole, we will end up with 1.5 moles. The extra 0.5 moles are proportional to conversion:

$$n = n_0(1 + 0.5X) = n_0[1 + 0.5 - 0.5\exp(-kt)]$$

$$P = P_0[1.5 - 0.5\exp(-kt)]$$

$$1.5 - \frac{P}{P_0} = 0.5\exp(-kt)$$

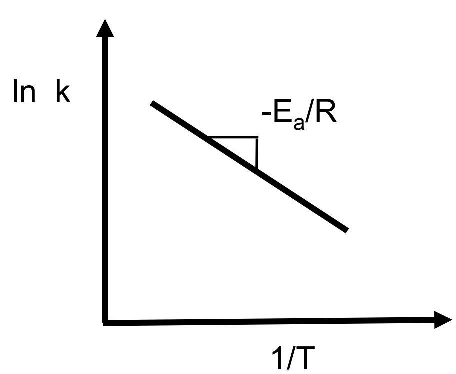
$$k = \frac{1}{t}\ln\left(\frac{1}{3 - 2\,P/P_0}\right)$$

With this, we can find k…

With Arrhenius we have:

$$k = \bar{A}\exp\left(-\frac{E_a}{RT}\right) \rightarrow \ln k = \ln\bar{A} - \frac{E_a}{RT}$$

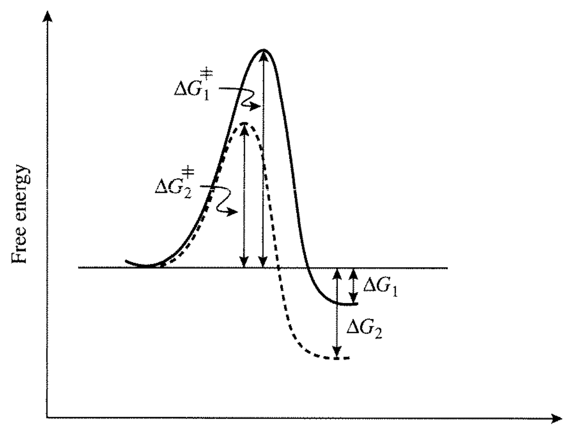
With that, you can determine E_a:



Problem 2
For similar reactions, trends in equilibrium constants can often be similar to trends in rate constants and thus can be used to predict each other. One approximation that can often be made for similar reactions is that the difference in transition state free energies is proportional to the difference in free energies of reaction:

$$\Delta G^{\ddagger}_{0,1} - \Delta G^{\ddagger}_{0,2} = \alpha\left(\Delta G_{0,1} - \Delta G_{0,2}\right)$$

For two similar reactions (for example, same reactants with different products):



Can you find a way to express the rate constants as a function of the equilibrium constants (and α) $f(k_1, k_2) = g(K_1, K_2)$?

Solution:
In class we saw that:

$$r = \frac{\bar{k}T}{h} \exp\left[\frac{\Delta S_0^{\ddagger}}{R}\right] \exp\left[-\frac{\Delta H_0^{\ddagger}}{RT}\right] C_A C_B$$

$$k_i = \frac{\bar{k}T}{h} \exp\left[\frac{\Delta S^{\ddagger}_{0,i}}{R}\right] \exp\left[-\frac{\Delta H^{\ddagger}_{0,i}}{RT}\right] = \frac{\bar{k}T}{h} \exp\left[\frac{\Delta S^{\ddagger}_{0,i}}{R} - \frac{\Delta H^{\ddagger}_{0,i}}{RT}\right]$$

From Thermo:
$\Delta G = \Delta H - T\Delta S$

$$k_i = \frac{\bar{k}T}{h} \exp\left[-\frac{\Delta G^{\ddagger}_{0,i}}{RT}\right]$$

$$\frac{k_1}{k_2} = \frac{\exp\left[-\frac{\Delta G_{0,1}^{\ddagger}}{RT}\right]}{\exp\left[-\frac{\Delta G_{0,2}^{\ddagger}}{RT}\right]} = \exp\left[-\frac{\Delta G_{0,1}^{\ddagger} - \Delta G_{0,2}^{\ddagger}}{RT}\right]$$

with: $\Delta G_{0,1}^{\ddagger} - \Delta G_{0,2}^{\ddagger} = \alpha\left(\Delta G_{0,1} - \Delta G_{0,2}\right)$

$$\frac{k_1}{k_2} = \exp\left[-\frac{\alpha\left(\Delta G_{0,1} - \Delta G_{0,2}\right)}{RT}\right]$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{\alpha\left(\Delta G_{0,1} - \Delta G_{0,2}\right)}{RT}$$

From Thermo:

$$-\frac{\Delta G_0}{RT} = \ln\mathrm{K}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \alpha(-\ln \mathrm{K}_1 + \ln\ \mathrm{K}_2) = \alpha \ln\left(\frac{K_2}{K_1}\right)$$

Problem 3
For the following reaction in series in a batch reactor at constant T, V and P:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Find the concentration of C as a function of time with $C_A(0) = C_{A,0}$ and $C_B(0) = C_C(0) = 0$.

Solution:

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

We integrate the first differential equation:

$$\frac{dC_A}{C_A} = -k_1 dt$$

$$\ln \frac{C_A}{C_{A,0}} = -k_1 t$$

$$C_A = C_{A,0} \exp(-k_1 t)$$

The second differential equation is:

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B = k_1 C_{A,0} \exp(-k_1 t) - k_2 C_B$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A,0} \exp(-k_1 t)$$

Here we have a linear first order inhomogeneous differential equation. We can find a general and particular solution and add them together:

The general solution satisfies:

$$\frac{dC_B}{dt} + k_2 C_B = 0$$

$Y_G = U \exp(-k_2 t)$ with U a constant.

To find a particular solution, let's try:

$Y_P = T\exp(-k_1 t)$ with T a constant.

We plug Y_P into the equation:

$$\frac{dY_P}{dt} + k_2 Y_P = -k_1 T\exp(-k_1 t) + k_2 T\exp(-k_1 t) = k_1 C_{A,0}\exp(-k_1 t)$$

$$\rightarrow T = \frac{k_1 C_{A,0}}{k_2 - k_1}$$

$$C_B = Y_P + Y_G = \frac{k_1 C_{A,0}}{k_2 - k_1}\exp(-k_1 t) + U\exp(-k_2 t)$$

@t=0 $C_B = 0$

$$\frac{k_1 C_{A,0}}{k_2 - k_1} + U = 0$$

$$C_B = \frac{k_1 C_{A,0}}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)]$$

Now let's find C_C. By mass balance, we know that:

$$C_{A,0} = C_A + C_B + C_C \rightarrow C_C = C_{A,0} - C_A - C_B$$

$$\begin{aligned} C_C &= C_{A,0} - C_{A,0}\exp(-k_1 t) - \frac{k_1 C_{A,0}}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \\ &= C_{A,0}\left(1 - \exp(-k_1 t) - \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)]\right) \end{aligned}$$