NAME: _____

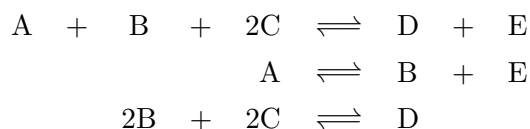| Instructions: The exam is closed book and closed notes. Write all answers on separate paper. Do not write any answers on the exam itself. Hand in your exam as well as your solution at the end. Make sure your name is on your solution and your exam. |
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Exercise 1. Stoichiometry. 25 pts.

(a) What is the difference between a set of reactions that is linearly independent and a set of reactions that is linearly dependent?

(b) For the reaction

$$2NO + O_2 \rightleftharpoons 2NO_2$$
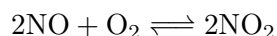
is it likely that this overall reaction would occur also as a molecular event? Why or why not?

(c) Consider the set of reactions

$$
\begin{array}{ccccccccc}
A & + & B & + & 2C & \rightleftharpoons & D & + & E \\
 & & & & A & \rightleftharpoons & B & + & E \\
2B & + & 2C & & & \rightleftharpoons & D & &
\end{array}
$$

1. Write out the species list and stoichiometric matrix. For ease of grading, please keep the species in alphabetical order in the species list.
2. By inspection, what is the rank of this matrix? Explain your answer.

Solution.

(a) For a linearly independent set of reactions, no reaction in the set can be expressed as a linear combination of the other reactions. For a linearly dependent set of reactions, at least one of the reactions can be expressed as a linear combination of the other reactions.

(b) No, as a molecular event this reaction is unlikely to occur because it requires the forming and breaking of many bonds to create and destroy five separate molecules in a single reaction event. The mechanism explaining this overall reaction is likely to involve several other simpler reactions that each require require fewer total molecules and formation and destruction of a smaller number of bonds.

(c)   1. Species list:
$$\boldsymbol{A} = \begin{bmatrix} A & B & C & D & E \end{bmatrix}^T$$

Stoichiometric matrix:
$$\boldsymbol{\nu} = \begin{bmatrix} -1 & -1 & -2 & 1 & 1 \\ -1 & 1 & 0 & 0 & 1 \\ 0 & -2 & -2 & 1 & 0 \end{bmatrix}$$

2. Add reactions 2 and 3 together and you obtain reaction 1 so the rank is less than 3. Reactions 2 and 3 are independent because 2 does not contain species C and 3 does. So the rank is greater than 1. Therefore the rank is 2.

$\square$

Exercise 2. Equilibrium, friend or foe? 25 pts.

The following reaction takes place at low pressure in the gas phase

$$A + B \rightleftharpoons C$$
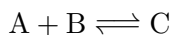
You charge a batch reactor with equal amounts of A and B and no C, run the reactor for a long time at a given temperature and pressure, and then open it up and find that you have converted about 50 percent of the starting materials.

But you need to reach 75 percent conversion for this process to be profitable. Your boss asks you to troubleshoot this process and make suggestions to save the project, which is about to be canceled. What do you tell your boss? Here are some options to consider. Feel free to choose one or more of these, or suggest your own options. The important point is to explain and justify your choice.

(a) Just run the reactor for a longer time. Eventually it will reach 75 percent conversion, guaranteed. You just have to be patient. State what other thermochemical data you require, if any, to justify this approach.

(b) Change the operating temperature. If you choose this option, what new temperature do you select? State what other thermochemical data you require, if any, to select the new temperature, and calculate the new temperature assuming whatever new data you require is available in your company's thermochemical database.

(c) Change the operating pressure. If you choose this option, what new pressure do you select? Again state what other thermochemical data, if any, you require to select the new pressure, and calculate the new pressure assuming whatever new data you require is available in your company's thermochemical database.

Solution. This is the same reaction stoichiometry that we examined in class. It leads to the equilibrium condition, assuming an idea gas,

$$K = \frac{1}{P} \frac{(y_{C0} + \varepsilon)(1 - \varepsilon)}{(y_{A0} - \varepsilon)(y_{B0} - \varepsilon)}$$

For the given starting conditions, this becomes

$$KP = \frac{\varepsilon(1 - \varepsilon)}{(1/2 - \varepsilon)^2}$$

We also have that the conversion is related to reaction extent by

$$x = \frac{n_{A0} - n_A}{n_{A0}} = \frac{\varepsilon}{(1/2)} = 2\varepsilon$$

So if the system were at equilibrium, fifty percent conversion means

$$\varepsilon = 1/4 \qquad K(T_1)P_1 = \frac{(1/4)(3/4)}{(1/4)^2} = 3$$

And 75 percent conversion means

$$\varepsilon = 3/8 \qquad K(T_2)P_2 = \frac{(3/8)(5/8)}{(1/8)^2} = 15$$

So we have to increase KP by a factor of 5. If we can do that, then we know that, at equilibrium, we will have 75 percent conversion.

But, in all cases, we still may need to speed up this reaction so that we approach equilibrium in a reasonable time, i.e., find a catalyst to increase the rate of the forward reaction.

(a) If you go down this path, you don't believe that the system had sufficient time to reach equilibrium in the first place. To justify the belief that you can reach 75 percent conversion, we have to determine that $KP \geq 15$. Because if it's less than 15, waiting won't help, because we won't *ever* reach 75 percent conversion. We know P, so we need to evaluate only K. Therefore we need ΔG^0 evaluated at the system temperature. We then check

$$KP \geq 15$$
$$e^{\frac{-\Delta G^0}{RT}} \geq 15/P$$
$$\Delta G^0 \leq -RT\ln(15/P)$$

So we look up ΔG^0 at the system T and see if this is true.

(b) It the system were initially at temperature T_1, to increase KP by factor 5 we require

$$K(T_2) = 5K(T_1) \qquad K(T_2)/K(T_1) = 5$$

So now we need the van 't Hoff equation, which gives for ΔH^0 roughly constant over the temperature range $[T_1, T_2]$,

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solving this equation for T_2 gives

$$T_2 = \left[\frac{1}{T_1} - \frac{R}{\Delta H^0}\ln(5)\right]^{-1}$$

We require ΔH^0 at the system T.

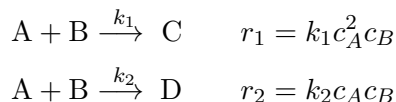(c) If the system was at initially at pressure P_1, to increase KP by factor 5, we require

$$P_2 = 5P_1$$

We do not require any further thermochemical data.

$\square$

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Exercise 3. Selectivity of competing first-order and second-order reactions. 50 pts.

The following two reactions take place in a constant-volume batch reactor

$$A + B \xrightarrow{k_1} C \qquad r_1 = k_1 c_A^2 c_B$$

$$A + B \xrightarrow{k_2} D \qquad r_2 = k_2 c_A c_B$$

There is a large excess of reactant B initially, and therefore we can assume that c_B is approximately constant throughout the batch time. Note that, despite the stoichiometry, the first reaction is second-order in A, but the second reaction is first-order in A.

(a) Write out the component balance for species A in the reactor. How does it simplify when noting that B is in large excess?

(b) Solve the component balance for $c_A(t)$. Check that your solution satisfies the initial condition.

(c) Draw a sketch of $c_A(t)$ versus t.

(d) How would you define the *instantaneous* selectivity of product C, s_C (production of C relative to consumption of A). Explain in physical terms what this selectivity is measuring.

(e) How would you define the *overall* selectivity of product C, S_C as a function of the batch time, t. Explain in physical terms what this selectivity is measuring.

Are the two selectivities you have defined the same for this application? Why or why not?

(f) How would you define overall conversion of A for this reactor, x_A? Explain in physical terms what this conversion is measuring.

Hint: if you need to integrate something like

$$\int \frac{dx}{(x+a)(x+b)}$$

and, since WolframAlpha is unreachable, instead notice that you can express

$$\frac{1}{(x+a)(x+b)} = \frac{1}{b-a}\left[\frac{1}{x+a} - \frac{1}{x+b}\right]$$

and you know how to integrate both terms on the right-hand side. This is called a partial fraction expansion, and you will use it later in CBE 470.

Solution.

(a) The component balance for A in a well-mixed batch reactor is

$$\frac{d}{dt}(c_A V_R) = R_A V_R = -(r_1 + r_2)V_R = -(k_1 c_A^2 c_B + k_2 c_A c_B)V_R$$

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Due to B's excess, $c_B(t) \approx c_{B0}$ so redefine $k_1 = k_1 c_{B0}, k_2 = k_2 c_{B0}$, and divide by constant V_R to obtain

$$\frac{d}{dt} c_A = -(k_1 c_A^2 + k_2 c_A) \qquad c_A(0) = c_{A0}$$

(b) The problem is separable, so rearrange to obtain

$$\frac{dc_A}{c_A(c_A + k_2/k_1)} = -k_1 dt$$

and integrate both sides between the limits

$$\int_{c_{A0}}^{c_A} \frac{dc_A}{c_A(c_A + k_2/k_1)} = -k_1 \int_0^t dt$$

Using the hint gives (for $a = 0$, $b = k_2/k_1$)

$$\frac{1}{k_2/k_1} \ln \left(\frac{c_A}{c_A + k_2/k_1} \right) \Bigg|_{c_{A0}}^{c_A} = -k_1 t$$

Substituting the limits gives

$$\ln \left(\frac{c_A}{c_{A0}} \frac{c_{A0} + k_2/k_1}{c_A + k_2/k_1} \right) = -k_2 t$$

Exponentiate both sides and multiply by the denominator to obtain

$$\frac{c_A}{c_{A0}} (1 + k_2/(k_1 c_{A0})) = e^{-k_2 t} \left(\frac{c_A}{c_{A0}} + k_2/(k_1 c_{A0}) \right)$$

Solving for c_A/c_{A0} gives

$$\frac{c_A}{c_{A0}} (1 + k_2/(k_1 c_{A0}) - e^{-k_2 t}) = e^{-k_2 t} k_2/(k_1 c_{A0})$$

$$\frac{c_A}{c_{A0}} = \frac{k_2/(k_1 c_{A0}) e^{-k_2 t}}{1 + k_2/(k_1 c_{A0}) - e^{-k_2 t}}$$

Note that $c_A(0) = c_{A0}$ and the initial condition is satisfied.

(c) The plot of $c_A(t)$ is shown in Figure 1

(d) The instantaneous selectivity of C (from A) is

$$s_C = \frac{R_C}{-R_A} = \frac{r_1}{r_1 + r_2} = \frac{k_1 c_A^2}{k_1 c_A^2 + k_2 c_A} = \frac{c_A}{c_A + (k_2/k_1)}$$

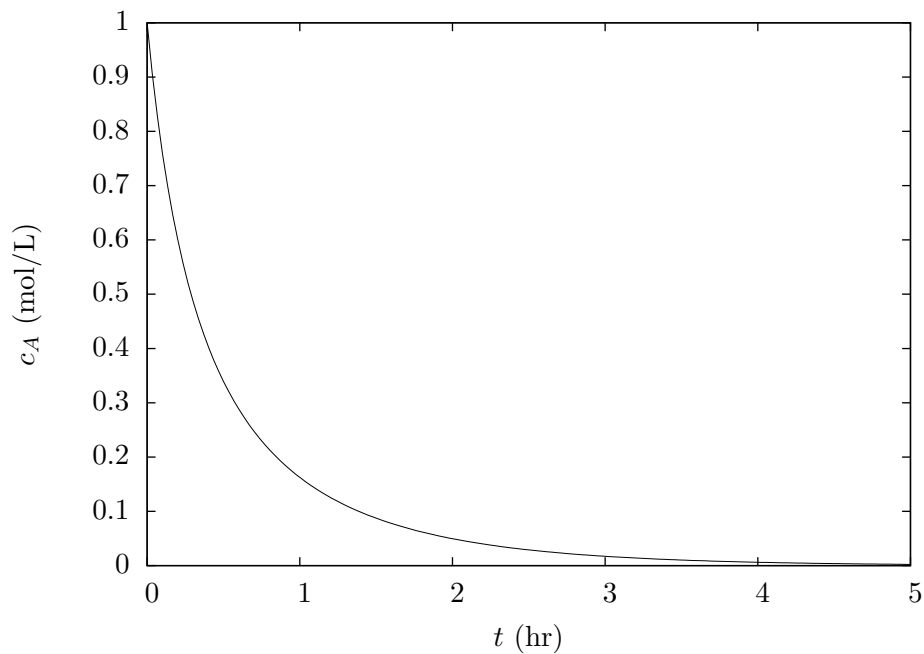This is the instantaneous fraction of A that is being converted to C.

Figure 1: Concentration of A versus time.

(e) The overall selectivity of C from A is

$$S_C = \frac{n_C - n_{C0}}{n_{A0} - n_A} = \frac{c_C - c_{C0}}{c_{A0} - c_A} \tag{1}$$

This is the fraction of A that is converted to C by time t.

Since the instantaneous selectivity varies with time (it depends on c_A, which varies with time), the overall selectivity is not equal to the instantaneous selectivity.

(f) The conversion of A is

$$x_A = \frac{n_{A0} - n_A}{n_{A0}} = 1 - \frac{c_A}{c_{A0}}$$

This is the fraction of A that has been converted to products (C and D).

$\square$