NAME: ______________________________

Instructions: The exam is **open** book and **closed** notes. Write your name on the exam. Work all the problems. You have 2 hours. Hand in your exam as well as your solution at the end.

Gas constant: $R = 82.06$ cm^3·atm/mol·K; $R = 1.987$ cal/mol·K

Problem 1. Nonisothermal PFR. 30 points

The reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$$

is carried out adiabatically in a series of tubular reactors with interstage cooling as shown in Figure 1. The feed is equimolar in A and B and enters each reactor at 27°C.

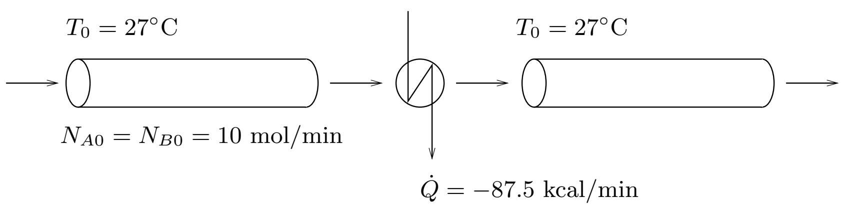

Figure 1: Tubular Reactors with Interstage Cooling.

The heat removed between the reactors is -87.5 kcal/min.

(a) What is the outlet temperature of the first reactor?

(b) What is the conversion of A at the outlet of the first reactor?

(c) Is the first reactor close to equilibrium at the exit?

State any assumptions that you make while solving the problem.
Data:

ΔH_R	-30 kcal/mol
C_p	25 cal/mol·K
K at 50°C	5.0×10^5
N_{A0}, N_{B0}	10 mol/min
$\dot{Q}$	-87.5 kcal/min

Problem 2. Changing catalyst and temperature. 30 points

The rate of a heterogeneously catalyzed, first-order reaction in a 0.75-cm diameter spherical pellet is $R_{Ap} = -3.2510^{-5}$ mol/cm^3·s when the catalyst is exposed to pure, gaseous A at a pressure of 1 atm and a temperature of 525 K. This reaction's activation energy is $E_a = 18,600$ cal/mol. Further, the effective diffusivity of A in the pellet is $D_A = 0.009$ cm^2/s at 525 K and that diffusion is in the regime of Knudsen flow. The bulk fluid and the external surface concentrations can be assumed the same. Find the rate of reaction if the catalyst is changed to a cylindrical pellet that is 0.5 cm in diameter and 1.0 cm in length, and the temperature is increased to 600 K.

Problem 3. A colleague's batch reactor energy balance. 40 points.

A colleague presents you with the following derivation of the energy balance for a constant-volume batch reactor.

> You know, the people writing our textbooks sure make things complicated. I found a much simpler energy balance for the constant-volume batch reactor. Here's how it goes. Because you cannot do work on a closed system at constant volume, the total energy balance is simply
>
> $$\frac{dU}{dt} = \dot{Q} \tag{1}$$
>
> For a single-phase system, internal energy $U(T, V, n_j)$ changes due to changes in T, V and n_j by
>
> $$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n_j} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n_j} dV + \sum_j \left(\frac{\partial U}{\partial n_j}\right)_{T,V,n_{k\neq j}} dn_j \tag{2}$$
>
> The definitions of constant volume heat capacity and partial molar internal energy are
>
> $$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n_j} \tag{3}$$
>
> $$\overline{U}_j = \left(\frac{\partial U}{\partial n_j}\right)_{T,V,n_{k\neq j}} \tag{4}$$
>
> Since the reactor volume is constant, $dV = 0$, and forming the time derivative of the internal energy from Equation 2 reduces to
>
> $$\frac{dU}{dt} = C_V \frac{dT}{dt} + \sum_j \overline{U}_j \frac{dn_j}{dt} \tag{5}$$

From the definition of enthalpy ($H = U + PV$), we know that

$$\overline{H}_j = \overline{U}_j + P\overline{V}_j \tag{6}$$

in which $\overline{H}_j$ is the partial molar enthalpy and $\overline{V}_j$ is the partial molar volume. The material balance for the batch reactor is

$$\frac{dn_j}{dt} = R_j V_R = \sum_i \nu_{ij} r_i V_R, \qquad j = 1, \ldots, n_s \tag{7}$$

in which r_i is the reaction rate per reactor volume and ν_{ij} is the stoichiometric coefficient for species j in reaction i. We can define the change in enthalpy and change in volume for reaction i by

$$\Delta H_{Ri} = \sum_{j=1}^{n_s} \nu_{ij}\overline{H}_j \qquad \Delta V_{Ri} = \sum_{j=1}^{n_s} \nu_{ij}\overline{V}_j \tag{8}$$

I put the material balance and these definitions in Equation 5 and I obtain

$$\boxed{C_V \frac{dT}{dt} = -\sum_i \left(\Delta H_{Ri} - P\Delta V_{Ri}\right) r_i V_R + \dot{Q}} \tag{9}$$

Notice my result doesn't agree with Equation 6.71 in our text!

$$\boxed{C_V \frac{dT}{dt} = -\sum_i \left[\Delta H_{Ri} - \alpha T V_R \sum_j \nu_{ij} \left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_k}\right] r_i V_R + \dot{Q}} \tag{6.71$'$}$$

And notice my result is much prettier, too. I wish these textbook writers would get it right for once!

Answer the following questions yes or no and provide a short justification.

(a) Is Equation 1 correct for the constant-volume batch reactor given the other assumptions?

(b) Is Equation 2 correct for this situation?

(c) Do Equations 3 and 4 agree with the usual definitions of constant-volume heat capacity and partial molar internal energy?

(d) Is Equation 5 a correct rearrangement of the previous equations?

(e) Is Equation 6 valid also for partial molar properties?

(f) Is Equation 7 a correct statement of the material balance for the batch reactor?

(g) Does Equation 8 agree with the usual definitions of enthalpy change and volume change upon reaction?

(h) Is Equation 9 a correct rearrangement of the previous equations?

(i) Provide a short discussion of the apparent energy balance contradiction.

If your answers to all questions above were yes, do you think the two energy balances are equivalent? If so, how would you show this equivalence?

If your answers to some of the questions above were no, how would you repair your colleague's derivation?