

CE 561, Exam 2, December 22, 1998

The exam consists of two problems, each containing multiple parts. You will have two hours to work on it. The point value of each part of each problem is indicated at the end of the problem statement. Note these values, and budget your time accordingly. You may use a single sheet of notes (8.5×11 inches, both sides). A portion of a table of integrals and a table of values of the exponential integral are attached to the exam for your use as well.

Good Luck!

- (1) Consider the production of SO₃ from SO₂ in a fixed bed tubular reactor. The overall reaction is SO₂ + ½ O₂ ↔ SO₃. The feed to the reactor is 3.0% by volume SO₂ and 97.0% by volume dry air (79% N₂, 21% O₂) at 400°C and 1.05 bar total pressure. The total feed flow rate is 2500 kg/hr. The reactor will be a 50 cm diameter cylindrical vessel filled with catalyst pellets. The platinum on alumina catalyst is in the form of 4 mm diameter cylindrical pellets (ranging from 15 to 50 mm long), with a catalyst density of 1.0 g cm⁻³, a pore volume of 0.4 cm³ g⁻¹, and a specific surface area of 150 m² g⁻¹. The density of the catalyst bed, as packed in the reactor, is 0.6 (kg catalyst)/m³. The pressure drop through the reactor is negligible. The reaction rate, in the absence of any diffusion limitations, is

$$r = k_1 C_{SO_2} - k_2 C_{SO_3}, \text{ with}$$

$$k_1 = 1.0 \times 10^6 e^{(-12000/T)} \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1} \text{ and } k_2 = 1.0 \times 10^{13} e^{(-24000/T)} \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}.$$

The specific heat of the gas mixture can be assumed constant at 1.0 kJ kg⁻¹ K⁻¹. The atomic weights of sulfur, oxygen, and nitrogen are 32, 16, and 14 g mol⁻¹, respectively.

- (a) Write the steady-state reactant (SO₂) mole balance equation and the enthalpy balance equation, including appropriate boundary conditions, for the fixed bed reactor for each of the following cases. Identify the variables in the equations and the units in which they are measured. Give their numerical values where possible. Where numerical values are not available from the problem statement, suggest how they might be obtained. For each part, give a **brief** description of how the balance equations could be solved numerically.

- (i) Ideal plug flow, no radial or axial mixing, no heat flow through the reactor walls. (10 points)

For ideal plug flow with no mixing, the mole balance on SO₂ can be written as

$$\frac{dF_{SO_2}}{dz} = -\rho_B \Omega (k_1 C_{SO_2} - k_2 C_{SO_3})$$

or it can be written as

$$\frac{d(u_s C_{SO_2})}{dz} = -\rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

The enthalpy balance can be written as

$$\rho_g \hat{c}_p u_s \frac{dT}{dz} = (-\Delta H_{rxn}) \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

The boundary conditions for these equations at the reactor inlet are $F_{SO_2} = F_{SO_2,o}$, or $C_{SO_2} = C_{SO_2,o}$ and $T = T_o$ at $z = 0$.

The variables in these equations are

F_{SO_2} = molar flow rate of SO_2 (mol s^{-1})

z = axial position in the reactor (m)

ρ_B = catalyst bed density = 0.6 ($\text{kg catalyst m}^{-3}$)

Ω = reactor cross-sectional area = 0.196 m^2

k_1 = forward first-order rate constant = $1.0 \times 10^6 e^{(-12000/T)}$ $\text{m}^3 \text{s}^{-1}$ (kg catalyst) $^{-1}$

k_2 = reverse first-order rate constant = $1.0 \times 10^{12} e^{(-24000/T)}$ $\text{m}^3 \text{s}^{-1}$ (kg catalyst) $^{-1}$

C_{SO_2} = concentration of SO_2 (mol m^{-3})

C_{SO_3} = concentration of SO_3 (mol m^{-3}). It is related to the concentration of SO_2 by stoichiometry. The molar flow rates are related by $F_{SO_3} = F_{SO_{2,o}} - F_{SO_2}$. The molar flow rate is the concentration times the velocity times the reactor cross-sectional area. So, we can relate the concentrations by $C_{SO_3} = \frac{u_{s,o}}{u_s} C_{SO_{2,o}} - C_{SO_2}$

u_s = superficial velocity (volumetric flow rate/reactor cross-sectional area) (m s^{-1})
This is the total molar flow rate divided by the total concentration (which can be determined from the ideal gas law) divided by the reactor cross-sectional area. This is

$$u_s = \frac{F_{N_2} + F_{O_2} + F_{SO_2} + F_{SO_3}}{\Omega} \left(\frac{RT}{p} \right) = \frac{F_{N_{2,o}} + F_{O_{2,o}} + F_{SO_{2,o}} - \frac{1}{2}(F_{SO_{2,o}} - F_{SO_2})}{\Omega} \left(\frac{RT}{p} \right)$$

$$u_s = u_{s,o} \frac{F_{N_{2,o}} + F_{O_{2,o}} + \frac{1}{2}F_{SO_{2,o}} - \frac{1}{2}F_{SO_2}}{F_{N_{2,o}} + F_{O_{2,o}} + F_{SO_{2,o}}} \left(\frac{T}{T_o} \right)$$

ρ_g = gas density (kg m^{-3}) This can be calculated from the ideal gas law as

$$\rho_g = \frac{\bar{M}p}{RT} = \rho_{g,o} \frac{\bar{M}T_o}{\bar{M}_o T} = \rho_{g,o} \left(\frac{F_{N_{2,o}} + F_{O_{2,o}} + F_{SO_{2,o}}}{F_{N_{2,o}} + F_{O_{2,o}} + \frac{1}{2}F_{SO_{2,o}} - \frac{1}{2}F_{SO_2}} \right) \frac{T_o}{T}$$

\hat{c}_p = specific heat of gas mixture = 1.0 $\text{kJ kg}^{-1} \text{K}^{-1}$

T = temperature (K)

ΔH_{rxn} = heat of reaction = forward activation energy – reverse activation energy = $-12000 \text{ R} = -99.8$ kJ mol^{-1}

\bar{M}_o = mean molecular weight of the feed (kg mol^{-1}) = $0.03 \cdot 0.064 + 0.97 \cdot 0.79 \cdot 0.028 + 0.97 \cdot 0.21 \cdot 0.032 = 0.0299$ kg mol^{-1}

F_o = total molar flow rate of the feed = 2500 $\text{kg hr}^{-1} / 3600$ $\text{s hr}^{-1} / (0.0299$ $\text{kg mol}^{-1}) = 23.23$ mol s^{-1}

$$\rho_{g,o} = \text{density of the feed stream} = \frac{\bar{M}_o p}{RT_o} = \frac{(0.0299)(105000)}{(8.314)(673)} = 0.561 \frac{\text{kg}}{\text{m}^3}$$

\bar{M} = mean molecular weight (kg mol^{-1})

$$= 0.028F_{N_2} + 0.032F_{O_2} + 0.064F_{SO_2} + 0.080F_{SO_3}$$

$F_{SO_{2,o}}$ = feed molar flow rate of SO_2 = $0.03 \cdot 23.23 = 0.70$ mol s^{-1}

$F_{O_{2,o}}$ = feed molar flow rate of O_2 = $0.97 \cdot 0.21 \cdot 23.23 = 4.73$ mol s^{-1}

$F_{N_{2,o}}$ = feed molar flow rate of N_2 = $0.97 \cdot 0.79 \cdot 23.23 = 17.80$ mol s^{-1}

$C_{SO_{2,o}}$ = feed concentration of SO_2 = $0.03 \cdot \text{total concentration} = 0.03 \cdot (p/RT) = 0.03 \cdot (10500/8.314/673) = 0.0563$ mol m^{-3}

$T_o = \text{feed temperature} = 400 \text{ }^\circ\text{C} = 673.15 \text{ K}$

$u_{s,o} = \text{the inlet superficial velocity (m s}^{-1}\text{)}. \text{ It can be calculated as the volumetric flowrate divided by the cross-sectional area at inlet conditions. This gives } u_{s,o} = 23.23 * 8.314 * 673 / 105000 / 0.196 = 6.32 \text{ m s}^{-1}\text{.}$

Mathematically, these balance equations form an initial value problem. They can be solved using one of the Euler methods, a Runge-Kutta method, Gear's method, or any of the other methods that we learned for 1st order ODE's.

- (ii) Plug flow with mixing in the axial direction due to flow around the catalyst pellets, but still no heat flow through the reactor walls. (5 points)

If we also consider axial mixing, then the equations become

$$\frac{d(u_s C_{SO_2})}{dz} = \frac{d}{dz} \left(D_{e,z} \frac{dC_{SO_2}}{dz} \right) - \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

and

$$\rho_g \hat{c}_p u_s \frac{dT}{dz} = \frac{d}{dz} \left(\lambda_{e,z} \frac{dT}{dz} \right) + (-\Delta H_{rxn}) \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

Now boundary conditions are needed at both the inlet and the outlet of the reactor.

These could be $C_{SO_2} = C_{SO_2,o}$ and $T = T_o$ at $z = 0$ and $\frac{dC_{SO_2}}{dz} = 0$ and $\frac{dT}{dz} = 0$ at $z = L$, or they could be the 'Danckwerts' boundary conditions,

$$u_s C_{SO_2} - D_{e,z} \frac{dC_{SO_2}}{dz} = u_{s,o} C_{SO_2,o} \text{ and } \rho \hat{c}_p u_s T - \lambda_{e,z} \frac{dT}{dz} = \rho_o \hat{c}_p u_{s,o} T_o \text{ at } z = 0 \text{ and } \frac{dC_{SO_2}}{dz} = 0 \text{ and } \frac{dT}{dz} = 0 \text{ at } z = L.$$

The variables are defined as in part (i). New variables are

$D_{e,z} = \text{effective axial dispersion coefficient (m}^2 \text{ s}^{-1}\text{)}. \text{ No value for this is given. It is best found by performing a tracer experiment.}$

$\lambda_{e,z} = \text{effective axial thermal conductivity (kJ m}^{-1} \text{ s}^{-1} \text{ K}^{-1}\text{)}. \text{ No value for this is given. It is best found from experiment.}$

$L = \text{the total length of the reactor}$

Mathematically, these equations give a 1-dimensional boundary value problem. It would be solved by replacing the derivatives with finite differences, then using Newton's method to solve the resulting set of algebraic equations.

- (iii) Plug flow with both radial and axial mixing due to flow around the catalyst pellets and heat transfer through the reactor wall to condensing steam at 200 °C. (5 points)

If we also consider radial mixing, then the equations become

$$\frac{\partial(u_s C_{SO_2})}{\partial z} = \frac{\partial}{\partial z} \left(D_{e,z} \frac{\partial C_{SO_2}}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r D_{e,r} \frac{\partial C_{SO_2}}{\partial r} \right) - \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

and

$$\rho_g \hat{c}_p u_s \frac{\partial T}{\partial z} = \frac{\partial}{\partial z} \left(\lambda_{e,z} \frac{\partial T}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r \lambda_{e,r} \frac{\partial T}{\partial r} \right) + (-\Delta H_{rxn}) \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

With inlet and outlet boundary conditions:

$$u_s C_{SO_2} - D_{e,z} \frac{\partial C_{SO_2}}{\partial z} = u_{s,o} C_{SO_2,o} \quad \text{and} \quad \rho \hat{c}_p u_s T - \lambda_{e,z} \frac{\partial T}{\partial z} = \rho_o \hat{c}_p u_{s,o} T_o \quad \text{at } z = 0$$

and $\frac{\partial C_{SO_2}}{\partial z} = 0$ and $\frac{\partial T}{\partial z} = 0$ at $z = L$.

and radial boundary conditions

$$\frac{\partial C_{SO_2}}{\partial r} = 0 \quad \text{and} \quad \frac{\partial T}{\partial r} = 0 \quad \text{at } r = 0$$

and $\frac{\partial C_{SO_2}}{\partial r} = 0$ and $-\lambda_{e,r} \frac{\partial T}{\partial r} = h_f (T - T_r)$ at $r = R_t$

The variables are defined as in parts (i) and (ii). New variables are

$D_{e,r}$ = effective radial dispersion coefficient ($\text{m}^2 \text{s}^{-1}$). No value for this is given. It is best found from experiment.

$\lambda_{e,r}$ = effective radial thermal conductivity ($\text{kJ m}^{-1} \text{s}^{-1} \text{K}^{-1}$). No value for this is given. It is best found from experiment.

R_t = the tube radius = 0.25 m

h_f = heat transfer coefficient from the fluid near the wall to the condensing steam ($\text{kJ s}^{-1} \text{K}^{-1} \text{m}^{-2}$). This is not given. It could be determined from experiment or from correlations.

Mathematically, these equations give a 2-dimensional boundary value problem.

This would also be solved by replacing the derivatives with finite differences, then using Newton's method to solve the resulting set of algebraic equations. However, the problem would be larger and more complex than the 1-D problem in part (ii).

- (b) For *adiabatic operation* of the reactor with ideal plug flow and no radial or axial mixing, derive a relationship between the reactor temperature and the SO_2 conversion. Estimate the maximum temperature that could be reached in the reactor. What are the concentrations of SO_2 and SO_3 when this maximum temperature is reached? (10 points)

We start from the balance equations for the ideal adiabatic plug flow reactor given in part (a):

$$\frac{d(u_s C_{SO_2})}{dz} = -\rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

$$\rho_g \hat{c}_p u_s \frac{dT}{dz} = (-\Delta H_{rxn}) \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

From the overall continuity equation, we know that the product $\rho_g u_s$ is constant, and we are assuming that the heat of reaction and specific heat are constant, so we can take these all inside the derivative in the energy equation and write

$$\frac{d}{dz}(u_s C_{SO_2}) = \frac{d}{dz} \left(\frac{\rho_g \hat{c}_p u_s}{\Delta H_{rxn}} T \right)$$

Integrating this (and using the values at the inlet) gives

$$u_s C_{SO_2} - u_{s,o} C_{SO_2,o} = \frac{\hat{c}_p \rho_{g,o} u_{s,o}}{\Delta H_{rxn}} (T - T_o)$$

Solving this for T gives

$$T = T_o + \frac{-\Delta H_{rxn}}{\rho_{g,o} \hat{c}_p} \left(C_{SO_2,o} - \frac{u_s}{u_{s,o}} C_{SO_2} \right)$$

If the reaction were irreversible, then the maximum temperature would be achieved when C_{SO_2} goes to zero. This would be

$$T_{\max,irrev} = 673.15 + \frac{99.8}{0.561 * 1.0} (0.0563) = 683.17 \text{ K}$$

The maximum possible temperature rise is 10 K. For this case, the factor $u_s/u_{s,o}$ would be

$$\frac{u_s}{u_{s,o}} = \frac{F_{N_2,o} + F_{O_2,o} + \frac{1}{2} F_{SO_2,o}}{F_{N_2,o} + F_{O_2,o} + F_{SO_2,o}} \left(\frac{T}{T_o} \right) = 0.985 \left(\frac{683}{673} \right) = 0.9996$$

This makes it clear that we can neglect this factor, and write our usual expression for a constant density adiabatic reactor,

$$T = T_o + \frac{-\Delta H_{rxn}}{\rho_{g,o} \hat{c}_p} (C_{SO_2,o} - C_{SO_2})$$

Since the reaction is reversible, we cannot, in fact, go to an SO_2 concentration of zero, but only to the equilibrium composition. The equilibrium composition is given by

$$k_1 C_{SO_2,eq} - k_2 C_{SO_3,eq} = 0, \text{ or } k_1 C_{SO_2,eq} = k_2 (C_{SO_2,o} - C_{SO_2,eq})$$

$$\text{from which } \frac{C_{SO_2,eq}}{C_{SO_2,o}} = \frac{k_2}{k_1 + k_2} = \frac{1}{1 + k_1/k_2} = \frac{1}{1 + 1 \times 10^{-7} e^{12000/T}}$$

At 673 K, this gives $\frac{C_{SO_2,eq}}{C_{SO_2,o}} = 0.153$, and at 683 K, this gives $\frac{C_{SO_2,eq}}{C_{SO_2,o}} = 0.190$, so we expect

to get between 81% and 85% conversion at equilibrium. 82% of the temperature rise for complete conversion would be 8.22 K, so we predict a maximum temperature for adiabatic operation of about 681.4 K. If we wanted to compute the temperature rise more precisely, we could substitute the expression for T into the expression for the equilibrium composition to get

$$\frac{C_{SO_2,eq}}{C_{SO_2,o}} = \frac{1}{1 + 1 \times 10^{-7} e^{\frac{12000}{673.15 + 10.02 \left(1 - \frac{C_{SO_2,eq}}{C_{SO_2,o}} \right)}}$$

and solve iteratively for $\frac{C_{SO_2,eq}}{C_{SO_2,o}}$. This would give $\frac{C_{SO_2,eq}}{C_{SO_2,o}} = 0.18326$ and $T_{\max} = 681.33 \text{ K}$

- (c) Calculate the Thiele modulus and estimate the effectiveness factor for the reaction at the reactor inlet temperature. The individual pellet may be considered isothermal. The effective diffusion coefficient (called D_{eA} in Froment and Bischoff) for SO_2 in the catalyst

pores is about $2.0 \text{ cm}^2 \text{ s}^{-1}$ at the feed temperature. For a reversible first-order reaction like the one considered here, the generalized Thiele modulus is

$$\phi_{rev} = \phi_{irrev} \sqrt{\frac{1 + k_1/k_2}{k_1/k_2}}$$

where ϕ_{rev} is the Thiele modulus for the 1st order reversible reaction, ϕ_{irrev} is the usual Thiele modulus for 1st order irreversible reaction, and k_1 and k_2 are the forward and reverse 1st order rate constants for the reaction. (10 points)

The usual Thiele modulus is given by

$$\phi = \frac{V}{S} \sqrt{\frac{k\rho_s}{D_{eA}}} = \frac{d_p}{4} \sqrt{\frac{k\rho_s}{D_{eA}}}$$

where d_p is the diameter of the catalyst pellets, and I have neglected the area on the ends of the pellets, since they are long and thin. Substituting in the numbers at the inlet temperature gives

$$\phi = \frac{0.004 \text{ m}}{4} \sqrt{\frac{1.0 \times 10^6 \exp(-12000/673.15) \text{ mol m}^3 (\text{kg catalyst})^{-1} \text{ s}^{-1} 1000 (\text{kg catalyst}) \text{ m}^{-3}}{2 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}}}$$

$$\phi = 0.30$$

For the reversible reaction, we then get

$$\phi_{rev} = 0.301 \sqrt{\frac{1 + 1 \times 10^{-7} e^{12000/673.15}}{1 \times 10^{-7} e^{12000/673.15}}} = 0.327 \text{ (reversibility of the reaction makes little difference).}$$

The effectiveness factor for a cylinder is given by an expression that contains Bessel functions, that you probably didn't have on your note sheet. However, we remember that for an arbitrary shape, with the Thiele modulus defined as it was here in terms of the volume to surface ratio, the effectiveness factor is approximately given by

$$\eta = \frac{\tanh \phi}{\phi}$$

which gives $\eta = 0.966$ for $\phi = 0.327$. Effects of pore diffusion limitations will be quite small.

- (d) Estimate the amount of catalyst and the reactor length (catalyst bed depth) required to produce 10^6 kg/year of SO_3 . After allowing for down time, a year of production is 8150 hours. (10 points)

Our feed stream contains 0.70 mol s^{-1} of SO_2 . If we achieved 100% conversion of SO_2 to SO_3 , this would give us $0.70 \text{ mol s}^{-1} = 0.056 \text{ kg s}^{-1}$ of SO_3 . So, 100% conversion of SO_2 to SO_3 would give $0.056 * 3600 * 8150 = 1.64 \times 10^6 \text{ kg/year}$ of SO_3 . Therefore, to get 10^6 kg/year of SO_3 , we need to achieve 61% conversion of the SO_2 . To find the residence time required to reach this conversion, we must integrate the SO_2 mole balance for the adiabatic plug flow reactor. This is

$$\frac{d(u_s C_{\text{SO}_2})}{dz} = -\rho_B (k_1 C_{\text{SO}_2} - k_2 C_{\text{SO}_3})$$

and we saw in part part (b) that changes in the superficial velocity would be negligible, so that we can define $\tau = z/u_s$ and write

$$\frac{dC_{SO_2}}{d\tau} = -\rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

Rearranging this and integrating it gives

$$\tau\rho_B = \int_{C_{SO_2,o}}^{C_{SO_2}} \frac{-dC_{SO_2}}{k_1 C_{SO_2} - k_2 C_{SO_3}} = \int_{C_{SO_2,o}}^{C_{SO_2}} \frac{-dC_{SO_2}}{k_1 C_{SO_2} - k_2 (C_{SO_2,o} - C_{SO_2})}$$

Letting $x = 1 - \frac{C_{SO_2}}{C_{SO_2,o}}$ and setting the limits to the desired 61% conversion, this becomes

$$\tau\rho_B = \int_0^{0.61} \frac{-dx}{k_1(1-x) - k_2x}$$

Substituting the expressions for the rate constants, this is

$$\tau\rho_B = \int_0^{0.61} \frac{-dx}{1 \times 10^6 \exp(-12000/T)(1-x) - 1 \times 10^{13} \exp(-24000/T)x}$$

From part (b), we have the relationship

$$T = T_o + \frac{-\Delta H_{rxn}}{\rho_{g,o} \hat{c}_p} (C_{SO_2,o} - C_{SO_2}) = 673.15 + 10.02x$$

Substituting this into the integral gives

$$\tau\rho_B = \int_0^{0.61} \frac{-dx}{1 \times 10^6 \exp\left(-\frac{12000}{673.15 + 10.02x}\right)(1-x) - 1 \times 10^{13} \exp\left(-\frac{24000}{673.15 + 10.02x}\right)x}$$

Oh no! We can't do this integral! But, we saw in part (b) that the reactor was almost isothermal. If it were isothermal, then the integral would just be

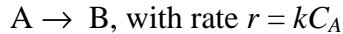
$$\tau\rho_B = \int_0^{0.61} \frac{-dx}{k_1(1-x) - k_2x} = \left[\frac{1}{k_1 + k_2} \ln(k_1(1-x) - k_2x) \right]_0^{0.61} = \frac{1}{k_1 + k_2} \ln\left(\frac{k_1}{0.39k_1 - 0.61k_2}\right)$$

The temperature goes from 673.15 K at $x = 0$ to 679.26 K at $x = 0.61$. At 673.15, the rate constants are $k_1 = 0.01811 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$, and $k_2 = 0.003281 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$. At 679.26, they are $k_1 = 0.02126 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$, and $k_2 = 0.004521 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$. The rate constants should be multiplied by the effectiveness factor from part (c) as well. That would give

$$\tau\rho_B = \frac{1}{\eta(k_1 + k_2)} \ln\left(\frac{k_1}{0.39k_1 - 0.61k_2}\right)$$

For isothermal operation at 673.15, this would give $\tau\rho_B = 33.5 \text{ s (kg catalyst) m}^{-3}$, and for isothermal operation at 679.26 K, this would give $\tau\rho_B = 26.3 \text{ s (kg catalyst) m}^{-3}$. So, a reasonable estimate is $\tau\rho_B = 30 \text{ s (kg catalyst) m}^{-3}$. Multiplying by the total feed rate of $1.238 \text{ m}^3 \text{ s}^{-1}$ gives a total catalyst requirement of 37.1 kg, which corresponds to a reactor volume of 0.0619 m^3 and a residence time of 0.05 s (50 ms). For the 50 cm diameter reactor, this gives a bed depth of 32 cm.

(2) The homogeneous, irreversible, exothermic, liquid phase reaction



is to be carried out in a well-mixed reactor. The available reactor has a volume of 1 m^3 . It is a simple stirred tank with no provision for heat addition or removal, so it must be run adiabatically. It can be run in batch mode (fill the reactor, run the reaction, drain the reactor, repeat) or in continuous mode (as a CSTR). The available feed stream contains 10 kgmol m^{-3} of species A and none of species B. It is at the ambient temperature of 300 K . It is available in unlimited quantities, so the goal is to process as much of it as possible with the given equipment. The density and specific heat of the feed are 1000 kg m^{-3} and $5 \text{ kJ kg}^{-1} \text{ K}^{-1}$, respectively. They may be considered independent of temperature and composition. The heat of reaction is -250 kJ mol^{-1} . The rate constant is $2 \times 10^{10} \exp(-10000/T) \text{ s}^{-1}$. It takes 5 minutes to fill the reactor and 10 minutes to drain the reactor.

$$\text{Helpful hints: } \int \frac{1}{x} \exp\left(\frac{a}{b-x}\right) dx = \text{Ei}\left(\frac{-a}{b-x}\right) - \exp\left(\frac{a}{b}\right) \text{Ei}\left(\frac{-ax}{b(b-x)}\right)$$

where $\text{Ei}(x)$ is the exponential integral.

The exponential integral may be expressed as the series

$$\text{Ei}(x) = e^{-x} \left(\frac{1}{x} - \frac{1}{x^2} + \frac{2!}{x^3} - \frac{3!}{x^4} + \frac{4!}{x^5} - \frac{5!}{x^6} + \dots \right)$$

which converges nicely with just a few terms when $\text{abs}(x) \gg 1$.

A table of values of the exponential integral for x from -10 to 10 is attached to the test.

- (a) What will be the average reactor throughput (kgmol of feed processed per hour) for each mode of operation (batch and continuous), and which mode of operation is preferable
 (i) if we require 60% conversion of A to B (outlet concentrations of 0.4 kgmol m^{-3} A and 0.7 kgmol m^{-3} B)? (10 points)

For the batch reactor, the material and energy balances are

$$\frac{dC_A}{dt} = -kC_A = -2 \times 10^{10} \exp\left(\frac{-10000}{T}\right) C_A$$

$$\frac{dT}{dt} = \left(\frac{-\Delta H}{\rho \hat{c}_p} \right) kC_A = 1 \times 10^{12} \exp\left(\frac{-10000}{T}\right) C_A$$

From these, we can get the usual relationship between concentration and temperature for an adiabatic reactor

$$T = T_o + \left(\frac{-\Delta H}{\rho \hat{c}_p} \right) (C_{A,o} - C_A) = 300 + 50(1 - C_A)$$

At 60% conversion, the temperature will increase from 300 K at $t = 0$, to 330 K at the end of the reaction time. Substituting the above expression into the material balance gives

$$\frac{dC_A}{dt} = -2 \times 10^{10} \exp\left(\frac{-10000}{300 + 50(1 - C_A)}\right) C_A$$

Rearranging and integrating this gives

$$t = \int_1^{0.4} \frac{dC_A}{-2 \times 10^{10} \exp\left(\frac{-10000}{300 + 50(1 - C_A)}\right) C_A} = \frac{1}{2 \times 10^{10}} \int_{0.4}^1 \frac{1}{C_A} \exp\left(\frac{200}{7 - C_A}\right) dC_A$$

Using the hint given above, this gives

$$t = \left(\frac{1}{2 \times 10^{10}} \right) \left(\text{Ei} \left(\frac{-200}{7 - C_A} \right) - \exp \left(\frac{200}{7} \right) \text{Ei} \left(\frac{-200 C_A}{7(7 - C_A)} \right) \right) \Bigg|_{0.4}^{1.0}$$

$$t = \left(\frac{1}{2 \times 10^{10}} \right) (\text{Ei}(-33.333) - \text{Ei}(-30.3030) - 2.561 \times 10^{12} (\text{Ei}(-4.7619) - \text{Ei}(1.7316)))$$

Evaluating the exponential integral using table and the series expression gives

$$t = \left(\frac{1}{2 \times 10^{10}} \right) (-9.2737 \times 10^{12} + 4.9436 \times 10^{11} - 2.561 \times 10^{12} (-32.91 + 4.02))$$

$$t \approx 3300 \text{ s} = 55 \text{ minutes}$$

So, the total time per batch is about 70 minutes to process $1 \text{ m}^3 = 1000 \text{ kg}$ of feed, which contains 1 kgmol of A and therefore produces 0.6 kgmol of B. The average production rate is therefore $8.57 \times 10^{-3} \text{ kgmol}$ of B per minute = 0.51 kgmol of B per hour from 860 kg of feed per hour.

For continuous operation, the CSTR material and energy balance equations are

$$\frac{C_A - C_{A_o}}{\tau} = -k C_A = -2 \times 10^{10} \exp \left(\frac{-10000}{T} \right) C_A$$

$$\frac{T - T_o}{\tau} = \left(\frac{-\Delta H}{\rho \hat{c}_p} \right) k C_A = 1 \times 10^{12} \exp \left(\frac{-10000}{T} \right) C_A$$

We can combine these to get the same relationship between temperature and concentration for adiabatic operation that we had before

$$T = T_o + \left(\frac{-\Delta H}{\rho \hat{c}_p} \right) (C_{A,o} - C_A) = 300 + 50(1 - C_A)$$

For 60% conversion ($C_A = 0.4$) the reactor will operate at 330 K .

Substituting this into the material balance and solving for the required residence time gives

$$\tau = \frac{C_{A_o} - C_A}{k C_A} = \frac{1 - C_A}{2 \times 10^{10} \exp \left(\frac{-10000}{300 + 50(1 - C_A)} \right) C_A}$$

and for an exit concentration of $C_A = 0.4$, this gives

$$\tau = \frac{0.6}{2 \times 10^{10} \exp \left(\frac{-10000}{300 + 50(0.6)} \right) 0.4} = 1085 \text{ s} = 18.1 \text{ min}$$

Since the reactor volume is 1 m^3 , this means that we can process $1/18.1 = 0.0553 \text{ m}^3$ of feed per minute, or 3.32 m^3 of feed per hour. The production rate is therefore 1.99 kgmol of B per hour, from 3320 kg of feed per hour.

For 60% conversion of the reactant, the production rate is almost a factor of 4 higher for continuous operation than for batch operation.

(ii) if we require 99% conversion of A to B (outlet concentrations of $0.01 \text{ kgmol m}^{-3}$ A and $1.09 \text{ kgmol m}^{-3}$ B)? (10 points)

If we require 99% conversion of the reactant, then the batch time is given by

$$t = \left(\frac{1}{2 \times 10^{10}} \right) \left(\text{Ei} \left(\frac{-200}{7 - C_A} \right) - \exp \left(\frac{200}{7} \right) \text{Ei} \left(\frac{-200 C_A}{7(7 - C_A)} \right) \right) \Bigg|_{0.01}^{1.0}$$

$$t = \left(\frac{1}{2 \times 10^{10}} \right) (\text{Ei}(-33.333) - \text{Ei}(-28.6123) - 2.561 \times 10^{12} (\text{Ei}(-4.7619) - \text{Ei}(-0.040875)))$$

Evaluating this gives

$$t = \left(\frac{1}{2 \times 10^{10}} \right) (-9.2737 \times 10^{12} + 9.675 \times 10^{10} - 2.561 \times 10^{12} (-32.91 - 2.58))$$

$$t \approx 4100 \text{ s} = 68 \text{ minutes}$$

So, the total time per batch is about 83 minutes to process $1 \text{ m}^3 = 1000 \text{ kg}$ of feed, which contains 1 kgmol of A and therefore produces 0.99 kgmol of B. The average production rate is therefore $1.19 \times 10^{-2} \text{ kgmol of B per minute} = 0.72 \text{ kgmol of B per hour}$ from 720 kg of feed per hour.

For continuous operation, the necessary residence time for 99% conversion is

$$\tau = \frac{C_{A0} - C_A}{k C_A} = \frac{0.99}{2 \times 10^{10} \exp \left(\frac{-10000}{300 + 50(0.99)} \right) 0.01} = 13200 \text{ s} = 220 \text{ minutes}$$

Since the reactor volume is 1 m^3 , this means that we can process $1/220 = 0.00454 \text{ m}^3$ of feed per minute, or 0.273 m^3 of feed per hour. The production rate is therefore 0.27 kgmol of B per hour, from 270 kg of feed per hour.

For 99% conversion of the reactant, the production rate is almost a factor of 3 higher for batch operation than for continuous operation.

- (b) Based on the above results, it is proposed to run the reactor in continuous (CSTR) mode, with the residence time that, in part a(i), was found to give 60% conversion. Perform a linear stability analysis at the steady state corresponding to 60% conversion. What will happen if we try to run the reactor at these conditions? (15 points)

This steady state was for a residence time of 1085 s, with the reactor temperature at 330 K and the concentration of A at 0.4 kgmol m^{-3} . To perform the stability analysis, we must analyze the transient species mole balance and enthalpy balance equations. These are

$$\frac{dC_A}{dt} = \frac{C_{A0} - C_A}{\tau} - k C_A = \frac{1 - C_A}{1085} - 2 \times 10^{10} \exp \left(\frac{-10000}{T} \right) C_A$$

$$\frac{dT}{dt} = \frac{T_o - T}{\tau} + \left(\frac{-\Delta H}{\rho \hat{c}_p} \right) k C_A = \frac{300 - T}{1085} + 1 \times 10^{12} \exp \left(\frac{-10000}{T} \right) C_A$$

So, the jacobian of the equations is

$$J = \begin{bmatrix} -\frac{1}{1085} - 2 \times 10^{10} \exp \left(\frac{-10000}{T} \right) & -\frac{2 \times 10^{14}}{T^2} \exp \left(\frac{-10000}{T} \right) C_A \\ 1 \times 10^{12} \exp \left(\frac{-10000}{T} \right) & -\frac{1}{1085} + \frac{1 \times 10^{16}}{T^2} \exp \left(\frac{-10000}{T} \right) C_A \end{bmatrix}$$

Evaluating this for $C_A = 0.4 \text{ kgmol m}^{-3}$ and $T = 330 \text{ K}$ gives

$$J = \begin{bmatrix} -2.304 \times 10^{-3} & -5.077 \times 10^{-5} \\ 6.911 \times 10^{-2} & 1.616 \times 10^{-3} \end{bmatrix}$$

The eigenvalues of this matrix are the roots of

$$(-2.304 \times 10^{-3} - \lambda)(1.616 \times 10^{-3} - \lambda) + (5.077 \times 10^{-5})(6.911 \times 10^{-2}) = 0$$

$$\lambda^2 + 6.88 \times 10^{-4} \lambda - 2.145 \times 10^{-7} = 0$$

From which

$$\lambda = -3.44 \times 10^{-4} \pm \sqrt{(3.44 \times 10^{-4})^2 + 2.145 \times 10^{-7}}$$

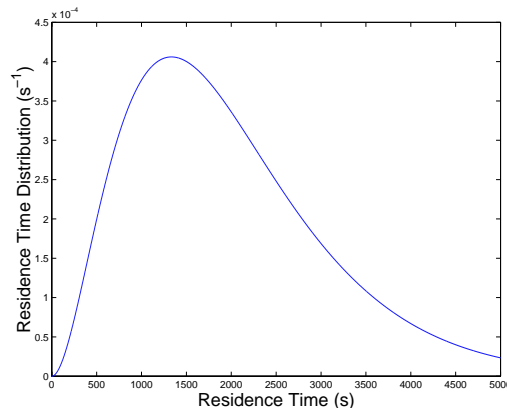
$$\lambda_1 = 2.33 \times 10^{-4} \text{ s}^{-1}, \text{ and } \lambda_2 = -9.21 \times 10^{-4} \text{ s}^{-1}$$

Since one of the eigenvalues is positive, this steady state is unstable. If we try to operate the reactor at this steady state by starting with this temperature and composition we will find that the reactor will move away from this steady state to another one with higher or lower conversion. In this case, the other two steady states correspond to about 13% conversion and about 72% conversion (but you didn't have to find those for this problem). Of course, if we can get the reactor to the high conversion steady state, that is even better than the 60% conversion steady state that we can't get to.

- (c) In an effort to get higher conversion in the continuous mode, the amount of mixing in the reactor was decreased (the impeller used for stirring was run at a slower speed). Under these conditions of high conversion, the reactor can be considered to be isothermal, at the adiabatic reaction temperature. For a feed rate of 0.5 kg s^{-1} , a tracer experiment was performed, and the residence time distribution was measured. It could be fit well by the expression

$$E(\theta) = 1.6875 \times 10^{-9} \theta^2 \exp\left(\frac{-3\theta}{2000}\right)$$

which is plotted below



Predict the outlet concentrations for the partially mixed reactor under these conditions. (15 points)

Using the segregated flow model, we integrate the conversion that would be obtained in a batch reactor after a time θ multiplied by the fraction of the flow that has residence time θ over all residence times. That is

$$\bar{C} = \int_0^{\infty} C(\theta)E(\theta)d\theta$$

For a first order reaction under isothermal conditions, $C(\theta) = C_0 \exp(-k\theta)$. The adiabatic reaction temperature is 350 K (as seen in part (a)), and at that temperature, the rate constant is $7.81 \times 10^{-3} \text{ s}^{-1}$. So, $C(\theta) = \exp(-7.81 \times 10^{-3} \theta)$, and the concentration coming out of the reactor is

$$\bar{C} = \int_0^{\infty} \exp(-7.81 \times 10^{-3} \theta) 1.6875 \times 10^{-9} \theta^2 \exp\left(\frac{-3\theta}{2000}\right) d\theta$$

$$\bar{C} = 1.6875 \times 10^{-9} \int_0^{\infty} \theta^2 \exp(-9.31 \times 10^{-3} \theta) d\theta$$

Either integrating by parts twice or using number 521 from the table of integrals (with $m = 2$) gives

$$\bar{C} = 1.6875 \times 10^{-9} \left[-\exp(-9.31 \times 10^{-3} \theta) \left(\frac{\theta^2}{9.31 \times 10^{-3}} + \frac{2\theta}{(9.31 \times 10^{-3})^2} + \frac{2}{(9.31 \times 10^{-3})^3} \right) \right]_0^{\infty}$$

$$\bar{C} = \frac{2 \times 1.6875 \times 10^{-9}}{(9.31 \times 10^{-3})^3} = 0.0042 \text{ kgmol m}^{-3}$$

Thus, we see that the partially mixed reactor gives almost 99.6% conversion with a residence time that is less than half of the residence time that we found for 99% conversion in a perfectly mixed reactor. The feed rate of 0.5 kg s^{-1} corresponds to 1800 kg hr^{-1} or $1.8 \text{ m}^3 \text{ hr}^{-1}$. So, we are producing $1.79 \text{ kgmol hr}^{-1}$ of B from 1800 kg hr^{-1} of feed. This is far better than either batch operation or continuous operation with perfect mixing at 99% conversion.

Values of the exponential integral

x	$Ei(x)$	x	$Ei(x)$	x	$Ei(x)$	x	$Ei(x)$	x	$Ei(x)$
-10.0	-2.4922E+03	-5.0	-4.0185E+01	-0.100	1.6228E+00	0.1	1.8229E+00	5.1	1.0213E-03
-9.9	-2.2816E+03	-4.9	-3.7332E+01	-0.096	1.6678E+00	0.2	1.2227E+00	5.2	9.0862E-04
-9.8	-2.0890E+03	-4.8	-3.4698E+01	-0.092	1.7146E+00	0.3	9.0568E-01	5.3	8.0861E-04
-9.7	-1.9130E+03	-4.7	-3.2264E+01	-0.088	1.7632E+00	0.4	7.0238E-01	5.4	7.1980E-04
-9.6	-1.7521E+03	-4.6	-3.0014E+01	-0.084	1.8139E+00	0.5	5.5977E-01	5.5	6.4093E-04
-9.5	-1.6050E+03	-4.5	-2.7934E+01	-0.080	1.8669E+00	0.6	4.5438E-01	5.6	5.7084E-04
-9.4	-1.4705E+03	-4.4	-2.6009E+01	-0.076	1.9223E+00	0.7	3.7377E-01	5.7	5.0855E-04
-9.3	-1.3475E+03	-4.3	-2.4227E+01	-0.072	1.9806E+00	0.8	3.1060E-01	5.8	4.5316E-04
-9.2	-1.2350E+03	-4.2	-2.2577E+01	-0.068	2.0419E+00	0.9	2.6018E-01	5.9	4.0390E-04
-9.1	-1.1320E+03	-4.1	-2.1048E+01	-0.064	2.1066E+00	1.0	2.1938E-01	6.0	3.6008E-04
-9.0	-1.0379E+03	-4.0	-1.9631E+01	-0.060	2.1753E+00	1.1	1.8599E-01	6.1	3.2109E-04
-8.9	-9.5173E+02	-3.9	-1.8316E+01	-0.056	2.2484E+00	1.2	1.5841E-01	6.2	2.8638E-04
-8.8	-8.7289E+02	-3.8	-1.7095E+01	-0.052	2.3266E+00	1.3	1.3545E-01	6.3	2.5547E-04
-8.7	-8.0075E+02	-3.7	-1.5961E+01	-0.048	2.4108E+00	1.4	1.1622E-01	6.4	2.2795E-04
-8.6	-7.3471E+02	-3.6	-1.4906E+01	-0.044	2.5019E+00	1.5	1.0002E-01	6.5	2.0343E-04
-8.5	-6.7426E+02	-3.5	-1.3925E+01	-0.040	2.6013E+00	1.6	8.6308E-02	6.6	1.8158E-04
-8.4	-6.1892E+02	-3.4	-1.3012E+01	-0.036	2.7107E+00	1.7	7.4655E-02	6.7	1.6211E-04
-8.3	-5.6824E+02	-3.3	-1.2161E+01	-0.032	2.8325E+00	1.8	6.4713E-02	6.8	1.4476E-04
-8.2	-5.2183E+02	-3.2	-1.1367E+01	-0.028	2.9701E+00	1.9	5.6204E-02	6.9	1.2928E-04
-8.1	-4.7932E+02	-3.1	-1.0626E+01	-0.024	3.1283E+00	2.0	4.8901E-02	7.0	1.1548E-04
-8.0	-4.4038E+02	-3.0	-9.9338E+00	-0.020	3.3147E+00	2.1	4.2614E-02	7.1	1.0317E-04
-7.9	-4.0470E+02	-2.9	-9.2860E+00	-0.016	3.5419E+00	2.2	3.7191E-02	7.2	9.2188E-05
-7.8	-3.7201E+02	-2.8	-8.6793E+00	-0.012	3.8336E+00	2.3	3.2502E-02	7.3	8.2387E-05
-7.7	-3.4204E+02	-2.7	-8.1103E+00	-0.008	4.2431E+00	2.4	2.8440E-02	7.4	7.3640E-05
-7.6	-3.1457E+02	-2.6	-7.5761E+00	-0.004	4.9402E+00	2.5	2.4915E-02	7.5	6.5831E-05
-7.5	-2.8939E+02	-2.5	-7.0738E+00	0.004	4.9482E+00	2.6	2.1850E-02	7.6	5.8859E-05
-7.4	-2.6630E+02	-2.4	-6.6007E+00	0.008	4.2591E+00	2.7	1.9182E-02	7.7	5.2633E-05
-7.3	-2.4512E+02	-2.3	-6.1544E+00	0.012	3.8576E+00	2.8	1.6855E-02	7.8	4.7072E-05
-7.2	-2.2569E+02	-2.2	-5.7326E+00	0.016	3.5739E+00	2.9	1.4824E-02	7.9	4.2104E-05
-7.1	-2.0786E+02	-2.1	-5.3332E+00	0.020	3.3547E+00	3.0	1.3048E-02	8.0	3.7666E-05
-7.0	-1.9150E+02	-2.0	-4.9542E+00	0.024	3.1763E+00	3.1	1.1494E-02	8.1	3.3700E-05
-6.9	-1.7649E+02	-1.9	-4.5937E+00	0.028	3.0261E+00	3.2	1.0133E-02	8.2	3.0155E-05
-6.8	-1.6271E+02	-1.8	-4.2499E+00	0.032	2.8965E+00	3.3	8.9390E-03	8.3	2.6986E-05
-6.7	-1.5005E+02	-1.7	-3.9210E+00	0.036	2.7827E+00	3.4	7.8910E-03	8.4	2.4154E-05
-6.6	-1.3843E+02	-1.6	-3.6053E+00	0.040	2.6813E+00	3.5	6.9701E-03	8.5	2.1621E-05
-6.5	-1.2775E+02	-1.5	-3.3013E+00	0.044	2.5899E+00	3.6	6.1604E-03	8.6	1.9356E-05
-6.4	-1.1793E+02	-1.4	-3.0072E+00	0.048	2.5068E+00	3.7	5.4478E-03	8.7	1.7331E-05
-6.3	-1.0892E+02	-1.3	-2.7214E+00	0.052	2.4306E+00	3.8	4.8202E-03	8.8	1.5519E-05
-6.2	-1.0063E+02	-1.2	-2.4421E+00	0.056	2.3604E+00	3.9	4.2671E-03	8.9	1.3898E-05
-6.1	-9.3002E+01	-1.1	-2.1674E+00	0.060	2.2953E+00	4.0	3.7794E-03	9.0	1.2447E-05
-6.0	-8.5990E+01	-1.0	-1.8951E+00	0.064	2.2346E+00	4.1	3.3489E-03	9.1	1.1150E-05
-5.9	-7.9538E+01	-0.9	-1.6228E+00	0.068	2.1779E+00	4.2	2.9688E-03	9.2	9.9881E-06
-5.8	-7.3601E+01	-0.8	-1.3474E+00	0.072	2.1246E+00	4.3	2.6329E-03	9.3	8.9485E-06
-5.7	-6.8135E+01	-0.7	-1.0649E+00	0.076	2.0744E+00	4.4	2.3360E-03	9.4	8.0179E-06
-5.6	-6.3102E+01	-0.6	-7.6988E-01	0.080	2.0269E+00	4.5	2.0734E-03	9.5	7.1848E-06
-5.5	-5.8466E+01	-0.5	-4.5422E-01	0.084	1.9820E+00	4.6	1.8410E-03	9.6	6.4388E-06
-5.4	-5.4193E+01	-0.4	-1.0477E-01	0.088	1.9393E+00	4.7	1.6352E-03	9.7	5.7709E-06
-5.3	-5.0256E+01	-0.3	3.0267E-01	0.092	1.8987E+00	4.8	1.4530E-03	9.8	5.1727E-06
-5.2	-4.6625E+01	-0.2	8.2176E-01	0.096	1.8599E+00	4.9	1.2915E-03	9.9	4.6369E-06
-5.1	-4.3276E+01	-0.1	1.6228E+00	0.100	1.8229E+00	5.0	1.1483E-03	10.0	4.1570E-06

Some useful indefinite integrals (from the CRC handbook of Chemistry and Physics)

$$517. \int e^x dx = e^x$$

$$518. \int e^{-x} dx = -e^{-x}$$

$$519. \int e^{ax} dx = \frac{e^{ax}}{a}$$

$$520. \int x e^{ax} dx = \frac{e^{ax}}{a^2}(ax - 1)$$

$$521. \int x^m e^{ax} dx = \begin{cases} \frac{x^m e^{ax}}{a} - \frac{m}{a} \int x^{m-1} e^{ax} dx \\ \text{or} \\ e^{ax} \sum_{r=0}^m (-1)^r \frac{m! x^{m-r}}{(m-r)! a^{r+1}} \end{cases}$$

$$522. \int \frac{e^{ax} dx}{x} = \log x + \frac{ax}{1!} + \frac{a^2 x^2}{2 \cdot 2!} + \frac{a^3 x^3}{3 \cdot 3!} + \dots$$

$$523. \int \frac{e^{ax}}{x^m} dx = -\frac{1}{m-1} \frac{e^{ax}}{x^{m-1}} + \frac{a}{m-1} \int \frac{e^{ax}}{x^{m-1}} dx$$

$$524. \int e^{ax} \log x dx = \frac{e^{ax} \log x}{a} - \frac{1}{a} \int \frac{e^{ax}}{x} dx$$

$$525. \int \frac{dx}{1+e^x} = x - \log(1+e^x) = \log \frac{e^x}{1+e^x}$$

$$526. \int \frac{dx}{a+be^{px}} = \frac{x}{a} - \frac{1}{ap} \log(a+be^{px})$$

$$527. \int \frac{dx}{ae^{mx} + be^{-mx}} = \frac{1}{m\sqrt{ab}} \tan^{-1} \left(e^{mx} \sqrt{\frac{a}{b}} \right), \quad (a > 0, b > 0)$$

$$528. \int \frac{dx}{ae^{mx} - be^{-mx}} = \begin{cases} \frac{1}{2m\sqrt{ab}} \log \frac{\sqrt{a} e^{mx} - \sqrt{b}}{\sqrt{a} e^{mx} + \sqrt{b}} \\ \text{or} \\ \frac{-1}{m\sqrt{ab}} \tanh^{-1} \left(\sqrt{\frac{a}{b}} e^{mx} \right), \quad (a > 0, b > 0) \end{cases}$$