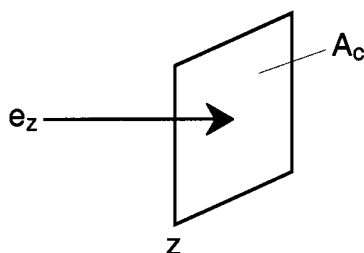


R11.3. Diffusion and Reaction Facilitated Heat Transfer

When diffusion is coupled with a reversible reaction contained between two surfaces, there is an increase in the rate of energy exchange between the two surfaces.

R11.3.A. Fundamentals of The Energy Flux

Consider the flux of energy, e_z , across the plane of area A_c shown below.



Ignoring any radiative heat transfer, the energy crossing the plane is the sum of the conductive energy transport, Q , and convective transport resulting from the flow of all the components, $\sum F_j H_j$.

$$\text{Energy crossing the plane} = Q + \sum F_j H_j$$

Where: F_j = molar flow rate of component j , (mol/s)

H_j = enthalpy of component j , (kJ/mol)

Q = conductive heat flow, (kJ/s)

If one now divides by the area, A_c , of the plane, the energy flux, e , is

$$\boxed{e = q + \sum W_j H_j} \quad (\text{R11.3-1})$$

Where: q = conductive transport = Q/A_c

$$q = -k\nabla T, \quad \left(\frac{\text{kJ}}{\text{s m}^2} \right) \quad (\text{R11.3-2})$$

The molar flux of A crossing the plane is

$$W_j = \frac{F_j}{A_c} = \text{molar flux of component } j, \text{ (mol/m}^2 \cdot \text{s)}$$

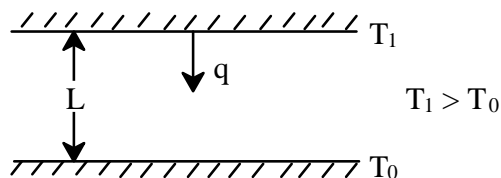
For species A

$$W_A = D_{AB} \frac{dy_A}{dz} + y_A (W_A + W_B) \quad (\text{R11.3-3})$$

In writing shell energy balances, one now only needs to consider the energy flux e .

R11.3.B. Conductive Heat Transfer

One means of accelerating conductive energy transport in a gas phase is by enthalpy transport.



Consider two horizontal parallel plates separated by a small distance, L . An inert non-reacting gas is contained between the two plates of which the top plate is heated and maintained at temperature T_1 and the bottom plate cooled and maintained at temperature T_0 . Energy is transported from the upper plate to the lower plate solely by conduction. For constant thermal conductivity, the heat flux is

$$q = \frac{k}{L}(T_1 - T_0) \quad (\text{R11.3-4})$$

We are neglecting any convective that might occur.

R11.3.C. Facilitated Heat Transfer

Consider what happens when the inert gas is replaced by a dissociating gas, e.g., N_2O_4 .



Near the upper, high-temperature plate, the equilibrium dictates that N_2O_4 will dissociate to form NO_2 while near the plate the lower temperature shifts the equilibrium so that the NO_2 reacts to form N_2O_4 . As a result the concentration of NO_2 will be higher at the upper plate than at the lower plate, while the concentration of N_2O_4 will be greater at the lower plate and less at the upper plate. These concentration gradients cause N_2O_4 to diffuse toward the upper plate and NO_2 molecules to diffuse toward the lower plate.

Consider the path of two molecules that have just been formed by the dissociation of one N_2O_4 molecule at the top plate. These two molecules diffuse toward the bottom plate where they combine to form one molecule of N_2O_4 . Because the reaction of 2NO_2 going to N_2O_4 is exothermic, the heat of reaction is released near the cooler plate. The N_2O_4 molecule then diffuses toward the upper plate where it dissociates to form NO_2 . This dissociation reaction is endothermic. Thus, energy is absorbed by the dissociation reaction at the top plate by the resulting molecules which diffuse to the bottom plate to release the energy upon recombination reaction at the

lower plate. The heat energy flux from the top to the bottom plate is substantially greater when the inert gas is replaced by a dissociating gas.

R11.3.D. Example of Diffusion and Reaction Facilitated Heat Transfer

Consider the one.-dimensional, steady-state transfer of energy through a gaseous binary mixture of NO_2 and N_2O_4 , a rapidly reacting system which has been studied experimentally for this enthalpy transport effect. Suppose that the mixture is confined between two horizontal, parallel, and inert solid walls ($0 \leq y \leq L$), the upper wall ($y = 0$) being at a higher temperature than the lower wall ($y = 0$), such that there is no tendency for natural convection to occur.

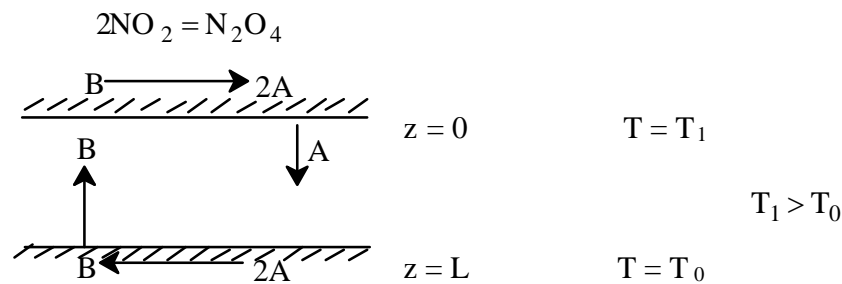
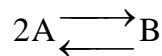
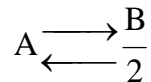


Figure RE11.3-1 Schematic of facilitated heat transfer

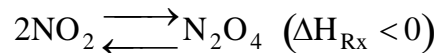


Taking A as our basis of calculating



Problem Statement

The following reaction takes place in between the two parallel plates shown in Figure R11.3-1.



Assuming that the reaction is at equilibrium everywhere, with

$$P_{\text{N}_2\text{O}_4} = K_P (P_{\text{NO}_2})^2 \quad (\text{RE11.3-1})$$

$$P_i = y_i P_{T0}$$

then

$$K_P P_{T0} = K = \frac{y_{\text{N}_2\text{O}_4}}{y_{\text{NO}_2}^2} = \frac{y_A}{y_B^2}$$

where y is mole fraction, and assuming that the gases behave ideally,

(a) derive an expression for the “effective” thermal conductivity k_{eff} at any point y , where

$$e_z = \text{energy flux} = -k_{\text{eff}} \frac{dT}{dz} \quad (\text{RE11.3-2})$$

such that $(k_{\text{eff}} - k)$, where k is the ordinary (or “frozen”) thermal conductivity of the (unreacting) gas mixture, is independent of composition (y_{NO_2}). Neglect sensible heat effects ($\Delta C_P = 0$) and take ΔH_R constant.

(b) Make a rough sketch of $(k_{\text{eff}} - k)$ vs. T indicating any peculiarities.

Solution

Vant Hoff's Law

$$\frac{d \ln K_{\text{eq}}}{dT} = \frac{d \ln K}{dT} = \frac{\Delta H_{\text{Rx}}}{RT^2} \quad (\text{RE11.3-3})$$

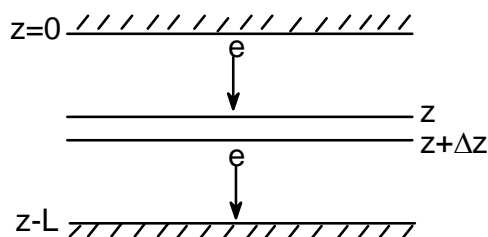
$$K = \frac{y_{\text{N}_2\text{O}_4}}{(y_{\text{NO}_2})^2} = \frac{y_{\text{B}}}{y_{\text{A}}^2} \quad (\text{RE11.3-4})$$

$$\frac{d \ln K}{dT} = \frac{\Delta H_{\text{Rx}}}{RT^2} \quad (\text{RE11.3-5})$$

Energy Balance

The energy flux is

$$e_z = q_z + \sum W_{jz} H_j \quad (\text{RE11.3-6})$$



Balancing a segment between z and $z + \Delta z$

$$e|_z - e|_{z+\Delta z} = 0 \quad (\text{RE11.3-7})$$

Divide by Δz and take the limit

$$\frac{de_z}{dz} = 0 \quad (\text{RE11.3-8})$$

Integrating

$$e_z = \text{constant} = -k \frac{\partial T}{\partial z} + W_{Az} H_A + W_{Bz} H_B \quad (\text{RE11.3-9})$$

For every mole of B that diffuses upward, 2 moles of A diffuse downward.

$$W_{Az} = -2W_{Bz}$$

$$e_z = -k \frac{\partial T}{\partial z} - W_A \frac{H_B}{2} - H_A = -\frac{kdT}{\partial z} - W_A \Delta H_{Rx}$$

where $W_A \equiv W_{Az}$

$$W_{zA} = -cD_{AB} \frac{dy_A}{dz} - \frac{W_A}{2} = \frac{-cD_{AB}}{\left(1 - \frac{y_A}{2}\right)} \frac{dy_A}{dz}$$

$$W_{zA} = \frac{-cD_{AB}}{1 - \frac{y_A}{2}} \frac{\partial y_A}{\partial z} \quad (\text{RE11.3-14})$$

The energy flux is

$$e = -k \frac{\partial T}{\partial z} + \frac{cD_{AB}}{1 - \frac{y_A}{2}} \Delta H_{Rx} \frac{\partial y_A}{\partial z} \quad (\text{RE11.3-15})$$

We now need to evaluate y_A at equilibrium

$$\frac{y_A^2}{y_B} = \frac{1}{K} = \frac{y_A^2}{1 - y_A} \quad (\text{RE11.3-16})$$

Solving for y_A

$$y_A = \frac{\sqrt{1 + 4K} - 1}{2K} \quad (\text{RE11.3-17})$$

Differentiating the mole fraction of A wrt z.

$$\frac{dy_A}{dz} = \frac{dy_A}{dK} \frac{dK}{dz} = \frac{\sqrt{1 + 4K} - (1 + 2K)}{2K^2 \sqrt{1 + 4K}} \frac{dK}{dz} \quad (\text{RE11.3-18})$$

Substituting (RE11.3-18) into (RE11-2.15)

$$e = -k \frac{dT}{dz} \left[\frac{cD_{AB}}{1 - \frac{y_A}{2}} \Delta H_{Rx} \frac{\sqrt{1+4K} - (1+2K)}{2K\sqrt{1+4K}} \frac{d \ln K}{dz} \right] \quad (\text{RE11.3-19})$$

Using Van't Hoffs Equation and the chain rule

$$\frac{d \ln K}{dz} = \frac{d \ln K}{dT} \frac{dT}{dz} = \frac{\Delta H_{Rx}}{RT^2} \frac{dT}{dz} \quad (\text{RE11.3-20})$$

$$e_z = -k \frac{dT}{dz} + \frac{cD_{AB}}{1 - \frac{\sqrt{1+4K} - 1}{4K}} \frac{\Delta H_{Rx}^2}{RT^2} \frac{\sqrt{1+4K} - (1+2K)}{2K\sqrt{1+4K}} \frac{dT}{dz}$$

$$e_z = -k_{\text{eff}} \frac{dT}{dz}$$

$$\boxed{(k_{\text{eff}} - k) = \frac{cD_{AB}\Delta H_{Rx}^2}{RT^2} \frac{1}{1+4K - \sqrt{1+4K}} \frac{1+2K - \sqrt{1+4K}}{\sqrt{1+4K}}} \quad (\text{RE11.3-21})$$

(1) As $T \rightarrow \infty$ (1) Then $K \rightarrow 0$ and $(k_{\text{eff}} - k) \rightarrow 0$

(2) As $T \rightarrow 0$ (2) Then $K \rightarrow \infty$ and $(k_{\text{eff}} - k) \rightarrow 0$

Note: (1) K goes almost to zero, albeit a very small constant

(2) Note $K \rightarrow 0$ faster than $\frac{1}{T^2} \rightarrow \infty$ so that (K/T^2) goes to zero.

We see the enhancement in the thermal conductivity goes through a maximum

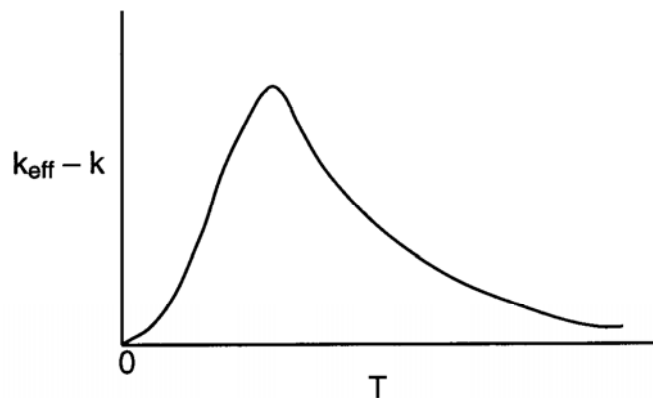


Figure RE11.3-2 Enhanced conductive heat transfer.

At high temperatures N_2O_4 is completely dissociated, or at low temperatures NO_2 is completely dimerized so that in these instances

$$k_{\text{eff}} \longrightarrow k$$

since the enthalpy exchange mechanism no longer occurs in a non-dissociating gas.