Heat Transfer in a Chemically Reacting System (Nitrogen Tetroxide-Dioxide)

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The effect of chemical reaction on heat transfer was investigated analytically for the dissociating system $N_2O_4 \rightleftharpoons 2NO_2$ in turbulent pipe flow. The Reynolds, Colburn, and Deissler analogies were adapted to reacting systems to determine local values of h'/h, the ratio of the heat transfer coefficient for a reacting system to that for the same system under frozen nonreacting conditions. The coefficient h' was determined by using effective thermal conductivities and heat capacities composed of a frozen and a reacting contribution. The equations for the effective properties, derived in this paper from heat transfer considerations, are in agreement with those developed from thermodynamics and statistical mechanics.

The effective properties vary significantly with temperature. Hence, the adaptation of Deissler's analogy, which was originally developed to consider the radial variation of physical properties across the pipe radius for an inert system, would be expected to give the most reliable results in this reacting system. In the range of variables studied it is found that the heat transfer coefficient for a reacting system may be as much as eighteen times the coefficient for a similar, frozen system. The results from the approximate Reynolds and Colburn analogies, which are evaluated by the use of mean physical properties, yield maximum values of h'/h of about 9.

The study covers a Reynolds number range of 10,000 to 200,000 and tube wall temperatures of 300° to 370°K.

Advances in the field of rocket propulsion have generated an increased interest in the study of heat transfer in chemically reacting systems. In such systems the total heat transfer may be increased owing to energy transfer by diffusion under the influence of a concentration gradient. The magnitude of the effect ranges from the case of a very slow reaction, where the effect of reaction on the heat transfer rate is negligible, to the very rapid reaction (where chemical equilibrium may be assumed), where the rate of diffusion controls the magnitude of the increase in heat transfer.

It is the purpose of this work to analyze theoretically the chemically reacting mixture nitrogen tetroxide-dioxide at atmospheric pressure. The system is an illustration of the extreme case where the kinetics do not enter into the analysis. The rate of reaction is sufficiently rapid that equilibrium is approached and the composition at any point in the system is dependent only upon the temperature at that point.

PREVIOUS WORK

Most of the previous work on this subject has involved the solution of the laminar boundary-layer equations for flat plates and blunt-nosed bodies by aerodynamicists. This interest arises because the laminar boundary on the nose cones of hypersonic missiles may, upon re-entry into the atmosphere, contain dissociated species which recombine outside the layer with the transfer of large amounts of heat. Moore (*12*), Metzdorf (*11*), Romig and Dore (*14*), Lees (*9*), Fay and Riddell (*6*), and Rose and Stark (*16*) studied heat transfer through a laminar layer of dissociated air. Rose, Probstein, and Adams (*15*) studied turbulent heat transfer through a cooled, dissociated boundary layer, correlating their experimental data with a modified form of the Colburn analogy. Altman and Wise (*1*), employing the von Karman analogy, obtained an expression relating equilibrium and frozen heat transfer rates for heat transfer from a flame to a cooled surface. They reported a 20.7% increase of heat transfer for liquid ammonia-gaseous oxygen when the equilibrium system was compared with the frozen system.

Studies of turbulent heat transfer in the nitrogen tetroxide-dioxide system flowing in pipes were conducted by Schotte (*18*), Beal and Lyerly (*2*), Brokaw (*4*), and Krieve and Mason (*8*). Schotte found that over-all heat transfer rates in the equilibrium system were six to eight times greater than in the frozen system. He proposed that the heat transfer coefficient could be obtained from a form of the Col-

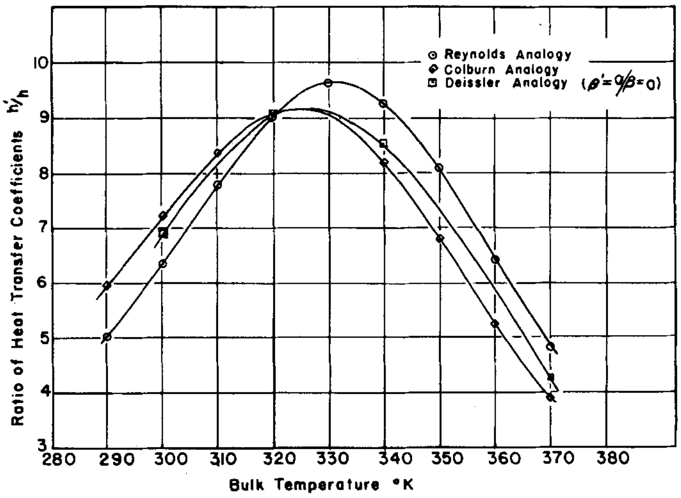

Fig. 1. Variation of h'/h as a function of bulk temperature (properties invariant).

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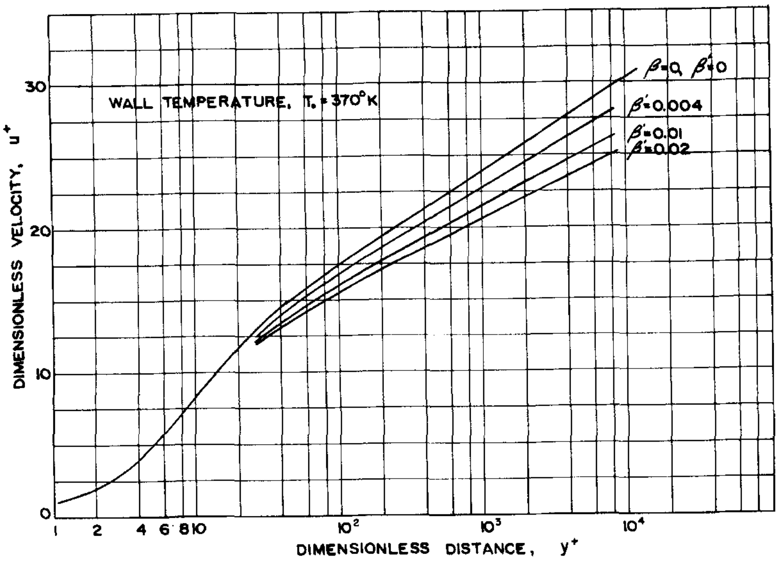

Fig. 2. Velocity profiles for 370°K. wall temperature.

burn analogy, in which temperature integrated thermal properties are employed. Brokaw analyzed the data of Beal and Lyerly and came to a somewhat similar conclusion, although the reference enthalpy method for obtaining the thermal properties was preferred. Krieve and Mason found that over-all heat transfer rates for the equilibrium system were as much as twelve times the rates for the frozen system. They also proposed that a Colburn type of relationship be used to evaluate the equilibrium, turbulent heat transfer coefficient using a reference enthalpy method for evaluating the effective thermal properties.

THEORETICAL DEVELOPMENT

All of the studies for turbulent flow in pipes have been concerned not with local coefficients but with over-all values applicable to the entire heat exchange equipment. Because of the sensitivity of the effective thermal properties to temperature it is difficult to use other than an empirical procedure for predicting the heat transfer coefficient. This explains the use of some kind of average, effective property such as that based upon the enthalpy.

The objective in the present work is to approach the problem from a different viewpoint, that is to evaluate local heat transfer coefficients applicable at one longitudinal position in the pipe. Then only radial variations in properties need be considered, and it is possible to take these variations into account in a semitheoretical fashion by using an analogy such as that proposed by Deissler (*5*) for inert systems. This is done in the next sections after expressions for the effective thermal conductivity and specific heat are first developed.

EFFECTIVE PROPERTIES IN REACTING SYSTEMS

The analogies between heat and momentum transfer for an inert fluid flowing in a pipe can be developed from the following equations for radial transfer per unit area:

$$\left.\begin{aligned} q &= -(k + \rho\, C_p\, \epsilon)\,\frac{dt}{dy} \\ &\text{or in molal form} \\ q &= -(k + \underline{\rho}\, \underline{C}_p\, \epsilon)\,\frac{dt}{dy} \end{aligned}\right\} \quad (1)$$

and

$$\tau = (\mu + \rho\, \epsilon)\,\frac{du}{dy} \quad (2)$$

When the fluid reacts chemically, the heat transfer is augmented owing to radial diffusion followed by reaction with the evolution of heat. Hence the total heat transfer is given by the sum of the contribution due to a temperature gradient and that due to the concentration gradient of reacting species. For example suppose a mixture of nitrogen tetroxide-dioxide is being heated as it flows through a pipe. As a result of the higher temperature near the tube wall the concentration of nitrogen dioxide will be greater near the wall. Hence nitrogen dioxide will diffuse toward the center of the tube and react. The contribution to the heat transfer rate will be equal to the rate of diffusion of nitrogen dioxide multiplied by the heat of reaction, or (N_{NO_2}) 1/2 $(\Delta H_{N_2O_4})$, where $(\Delta H_{N_2O_4})$ is the heat of dissociation of nitrogen tetraoxide. Since the type of diffusion involved is neither equimolal nor diffusion through a stagnant film, the general form of Fick's law (3) must be used. In these terms the rate of diffusion of nitrogen dioxide per unit area is

$$N_{NO_2} = x_{NO_2}(N_{N_2O_4} + N_{NO_2}) - \underline{\rho}\,(D + \epsilon)\,\frac{dx_{NO_2}}{dy} \quad (3)$$

The second term on the right includes both the molecular and turbulent contributions to the diffusion rate. Since the rates of diffusion of nitrogen dioxide and nitrogen tetroxide are related by the equation $N_{N_2O_4} = -1/2\, N_{NO_2}$, Equation (3) may be written as

$$N_{NO_2} = \frac{\underline{\rho}(D + \epsilon)}{\left(1 - \dfrac{x_{NO_2}}{2}\right)}\,\frac{dx_{NO_2}}{dy} \quad (4)$$

It is now possible to write an expression for the total heat transfer in a reacting system by summing the contribution due to a temperature difference [Equation (1)] and that due

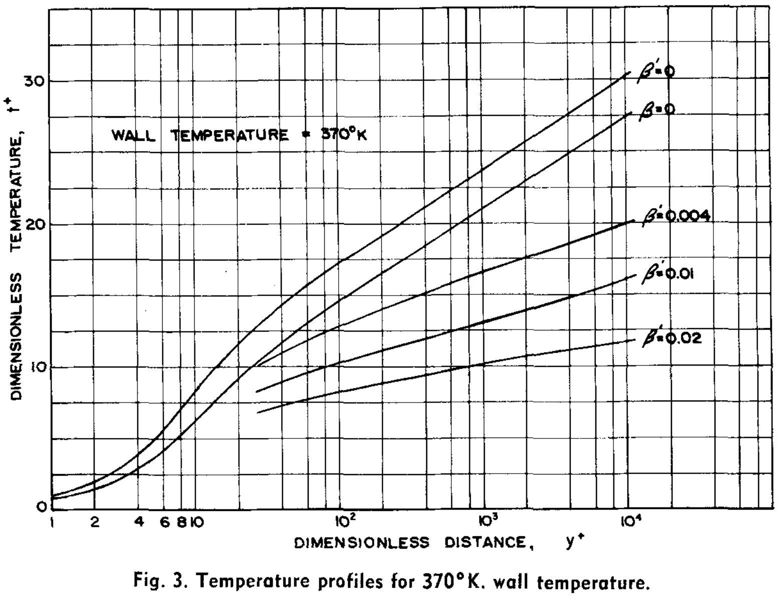

Fig. 3. Temperature profiles for 370°K. wall temperature.

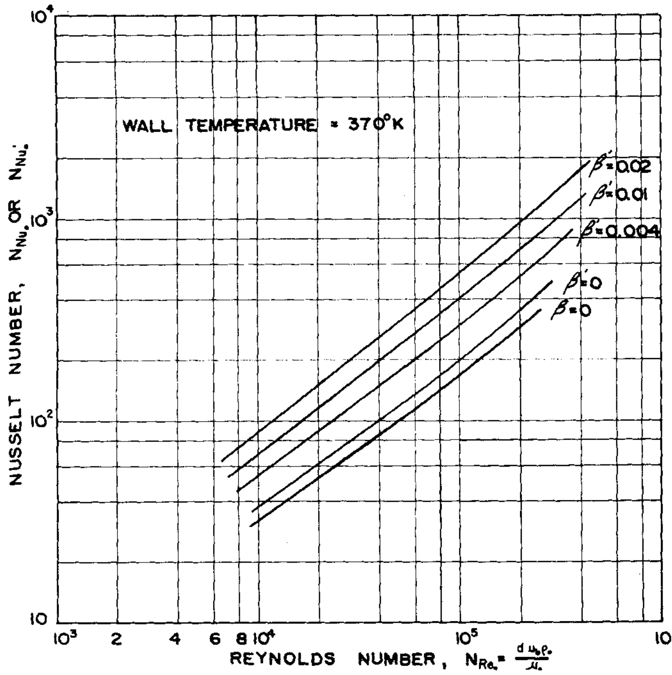

Fig. 4. Nusselt number vs. Reynolds number at 370°K. wall temperature.

to diffusion [Equation (4)]. The result is

$$q = -\left[k\frac{dt}{dy} + \frac{\Delta H_{N_2O_4}}{2}\,\frac{\underline{\rho}D}{\left(1-\frac{x_{NO_2}}{2}\right)}\,\frac{dx_{NO_2}}{dy} + \epsilon\underline{\rho}\,\underline{C}_p\frac{dt}{dy} + \frac{\Delta H_{N_2O_4}}{2}\,\frac{\underline{\rho}\,\epsilon}{\left(1-\frac{x_{NO_2}}{2}\right)}\,\frac{dx_{NO_2}}{dy}\right] \qquad (5)$$

In order to use the usual heat transfer analogies for reacting systems it is desirable to retain the form of Equation (1) by rewriting it as

$$q = -(k' + \rho\, C'_p\, \epsilon)\frac{dt}{dy} \qquad (6)$$

Equations (5) and (6) constitute two expressions for the total heat transfer rate. By equating the molecular transport terms in the two equations one sees that the effective thermal conductivity is given by

$$k' = k + \frac{\Delta H_{N_2O_4}}{2}\,\frac{\underline{\rho}D}{\left(1-\frac{x_{NO_2}}{2}\right)}\,\frac{dx_{NO_2}}{dt} \qquad (7)$$

By equating the turbulent transport terms one obtains an expression for the effective specific heat:

$$\underline{C}'_p = \underline{C}_p + \frac{\Delta H_{N_2O_4}}{2}\,\frac{1}{\left(1-\frac{x_{NO_2}}{2}\right)}\,\frac{dx_{NO_2}}{dt} \qquad (8)$$

In terms of the fraction of nitrogen tetroxide dissociated rather than the mole fraction, Equations (7) and (8) become

$$k' = k + \frac{\Delta H_{N_2O_4}}{(1+\alpha)}\,\underline{\rho}D\,\frac{d\alpha}{dt} \qquad (9)$$

$$\underline{C}'_p = \underline{C}_p + \frac{\Delta H_{N_2O_4}}{(1+\alpha)}\,\frac{d\alpha}{dt} \qquad (10)$$

The van't Hoff equation can be used to evaluate $d\alpha/dt$. When one assumes the ideal gas law, the equilibrium constant K is

$$K = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{x_{NO_2}{}^2}{x_{N_2O_4}}\pi = \frac{4-\alpha^2}{1-\alpha^2}\pi$$

If this is differentiated with respect to temperature, the result is

$$\frac{d\ln K}{dt} = \frac{2}{\alpha(1-\alpha^2)}\,\frac{d\alpha}{dt}$$

Using the van't Hoff equation to eliminate K one gets

$$\frac{d\alpha}{dt} = \frac{\Delta H_{N_2O_4}}{2\,RT^2}\,\alpha(1-\alpha^2) \qquad (11)$$

When one combines Equations (10), (11), and (9), the following results are obtained for k' and $\underline{C}'_p$:

$$k' = k + \frac{\Delta H^2_{N_2O_4}}{2\,RT^2}\,\underline{\rho}\,D\,\alpha(1-\alpha) \qquad (12)$$

$$\underline{C}'_p = \underline{C}_p + \frac{\Delta H^2_{N_2O_4}}{2\,RT^2}\,\alpha(1-\alpha) \qquad (13)$$

If Equations (12) and (13) are used to evaluate the thermal conductivity and specific heat, then Equations (2) and (6) can be employed as the starting point for developing analogies between heat and momentum transfer. Since Equations (2) and (6) are of the same form as expressions (2) and the molal form of (1), the results will be the usual analogies, such as Reynolds, von Karmans, or Deisslers, the only difference being that k' and $\underline{C}'_p$ are substituted for k and $\underline{C}_p$.

Equations (12) and (13) derived here from heat transfer considerations agree with those obtained by others (*4, 7, 10, 13*) from thermodynamics and statistical mechanics. For the binary system nitrogen tetroxide-dioxide the numerical evaluation of k' and C'_p does not pose serious difficulties. Brokaw (*4*) has combined the available theoretical and experimental data in a careful computation of effective properties. Some of his results at 1-atm. pressure are shown in Table 1, which covers a temperature range from 290° to 370°K. Within this interval the fraction (α) of nitrogen tetroxide dissociated varies from 0.137 to 0.858. Both effective and frozen values of k and C_p are tabulated, and it is immediately evident that the effective values range up to ten times as large as the

TABLE 1. COMPUTED PHYSICAL PROPERTIES FOR THE SYSTEM NITROGEN TETROXIDE-DIOXIDE*

Temp., °K.	α	$\mu \times 10^4$, poise	$k' \times 10^5$, cal./(sec.)(sq. cm.)(°C./cm.)	$k \times 10^5$, cal./(sec.)(sq. cm.)(°C./cm.)	$\rho \times 10^3$, g./cc.	C_p', cal/(g.)(°C.)	C_p, cal./(g.)(°C.)
290	0.137	1.124	20.083	3.110	3.414	1.0168	0.2017
300	0.199	1.192	25.668	3.337	3.130	1.2973	0.2042
310	0.283	1.270	31.176	3.587	2.832	1.6051	0.2060
320	0.395	1.356	35.233	3.860	2.540	1.8730	0.2075
330	0.518	1.445	36.366	4.143	2.272	2.0067	0.2083
340	0.590	1.534	33.977	4.427	2.043	1.9395	0.2089
350	0.710	1.615	29.086	4.693	1.864	1.6893	0.2094
360	0.803	1.689	23.308	4.938	1.726	1.3483	0.2099
370	0.858	1.754	18.037	5.163	1.621	1.0158	0.2106

* Pressure = 1 atm.

frozen C_p and k and also that they go through a maximum at an intermediate temperature.

REYNOLDS AND COLBURN ANALOGIES

When one makes the assumptions implied in Reynolds analogy, Equations (2) and (6) lead to the following expression for the Stanton number:

$$\frac{h'}{C'_p G} = a(N_{Re})^b \ldots\ldots \quad (14)$$

Dividing Equation (14) by its counterpart for the nonreacting or frozen system one gets for the ratio of the coefficients

$$\frac{h'}{h} = \frac{C'_p}{C_p} \ldots\ldots \quad (15)$$

By not making such drastic assumptions about the mechanism of heat transfer von Karman developed a more useful analogy which involved a function of the Prandtl number. Later Colburn proposed an analogy involving an empirical function of N_{Pr}. For a reacting system the Colburn result is

$$\frac{h'}{C'_p G} = a(N_{Re})^b \, (N'_{Pr'})^{-2/3} \quad (16)$$

In terms of the ratio of heat transfer coefficients Colburn's analogy suggests

$$\frac{h'}{h} = \frac{C'_p}{C_p} \left(\frac{N'_{Pr}}{N_{Pr}} \right)^{-2/3} \quad (17)$$

Both Reynolds and Colburns analogies assume that the physical property changes across the radius of the pipe are small enough that average values can be used. If the bulk mean temperature is used to evaluate the properties, h'/h is independent of the wall temperature and Reynolds number. Figure 1 depicts the ratio h'/h for these two analogies as evaluated from Equations (15) and (17) and the data in Table 1.

DEISSLERS ANALOGY

Because of the large variation of k' and C'_p with temperature the results of the previous two analogies are of doubtful accuracy. To have more confidence in the predictions a procedure should be used in integrating Equations (2) and (6) which takes into account the variation in C'_p, k' and also the density. Deissler's approach (5) developed for nonreacting systems with large property variations was adopted for the nitrogen tetroxide-dioxide case. The procedure requires representing the physical properties by temperature functions. Deissler originally used exponential equations, but for the nitrogen tetroxide-dioxide system it was found that more accurate representation could be obtained by linear expressions of the form

$$\frac{k'}{k'_o} \text{ or } \frac{C'_p}{C'_{p_o}}, \text{ etc.} = m\left(\frac{T}{T_o}\right) + b \quad (18)$$

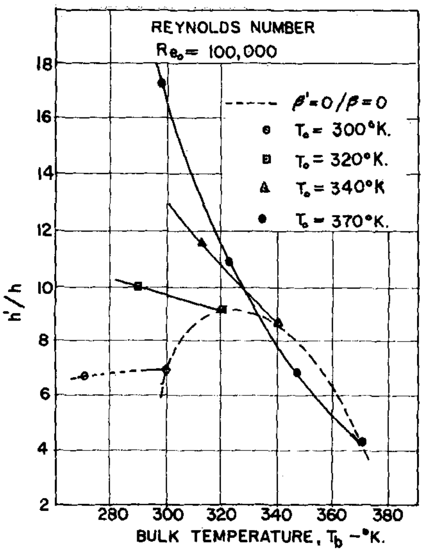

Fig. 5. Variation of h'/h with bulk temperature, variable properties.

The constants m and b were determined by least-mean-square procedures for each property. In some instances it was necessary to use two separate values of m and b to cover the required temperature range. The values of the constants and the accuracy with which they represent the physical property data are given in Table 2*. The poorest accuracy in using Equation (18) occurs for properties, such as C'_p, which pass through a maximum within the desired temperature range.

The solution of Equations (1) and (2) proposed by Deissler is well described in the literature (5) and need not be repeated. After one obtains velocity and temperature profiles, dimensionless, bulk mean values, t^+_b, and u^+_b are determined. The Reynolds and Nusselt numbers evaluated at the tube wall temperature can be related to these quantities by the expressions

$$N_{Re_o} = 2\, r^+_o \, u^+_b \quad (19)$$

$$N_{Nu_o} = \frac{2\, r^+_o \, N_{Pr_o}}{t^+_b} \quad (20)$$

In applying the procedure to the reacting system an IBM-650 computer was used to solve Equations (2) and (6) for velocity and temperature profiles, and these were integrated to obtain bulk mean values. Equation (19) was then employed to evaluate N_{Re_o}. The corresponding value of $N'_{Nu'_o}$ was evaluated from the modification of Equation (20) for a reacting system; that is

$$N'_{Nu'_o} = \frac{(2\, r^+_o)\, N'_{Pr'_o}}{(t^+_b)'} \quad (21)$$

In contrast to the analogies considered earlier Deisslers procedure introduces an additional parameter β as a measure of the heat transfer rate at the wall. The magnitude of q_o determines the temperature difference between the wall and the bulk fluid. These two temperatures determine the extent of property variations across the radius as indicated by Equation (18). Hence β is also a measure of the property changes in the fluid. Deissler defined β in terms of q_o in the following, dimensionless form:

$$\beta = \frac{q_o(\tau_o/\rho_o)^{1/2}}{c_{p_o}\, \tau_o\, T_o\, g_c} = \frac{1}{t^+}\left(1 - \frac{T}{T_o}\right) \quad (22)$$

where the latter equality arises from the definition of the dimensionless temperature. In applying Equation (22) to a reacting system the effective specific heat at the wall C'_{p_o} is substituted for C_{p_o}. This defines a β' for the reacting system analogous to β for the frozen system.

In order to obtain consistent heat transfer coefficient ratios, h'/h, it was necessary to determine N_{Nu_o} from Deisslers analogy for the frozen system. The frozen values of k and c_p given in Table 2 were used for this purpose.

The scope of the computations are best described in terms of the wall temperature and β' values. Calculations of $N'_{Nu'_o}$ and N_{Re_o} were made for the following conditions:

t_o — °K		
300°	$\beta = 0$,	$\beta' = 0$ and 0.004
320°	$\beta = 0$,	$\beta' = 0$ and 0.004
340°	$\beta = 0$,	$\beta' = 0$, 0.004
370°	$\beta = 0$,	$\beta' = 0$, 0.004, 0.01, and 0.02

Figures 2 and 3 for a wall temperature of 370°K. are illustrative of the dimensionless temperature and velocity profiles obtained. Figure 4 shows the corresponding curves of $N'_{Nu'_o}$ vs. N_{Re_o} for different values of β', and the curve of N_{Nu_o} vs. N_{Re_o} for $\beta = 0$ is included.

The curves in Figure 4 for $\beta' = 0$ and $\beta = 0$ constitute the Deissler type of analogy for constant physical properties, analogous to Reynolds and Colburn analogies. The ratio h'/h can be

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* Tabular material has been deposited as document 6529 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

obtained from $N'_{Nu_o'}$ and N_{Nu_o} read from these curves by the expression

$$\frac{N'_{Nu'_o}}{N_{Nu_o}} = \frac{\dfrac{h'd}{k_o'}}{\dfrac{hd}{k_o}} = \frac{h'}{h}\left(\frac{k_o}{k_o}\right)$$

or

$$\frac{h'}{h} = \frac{N'_{Nu'_o}}{N_{Nu_o}}\left(\frac{k_o'}{k_o}\right) \qquad (23)$$

The results of calculations from Equation (23) are indicated by the Deissler curve in Figure 1. Even though the Nusselt numbers are evaluated at the wall temperature in Equation (23), the restriction of $\beta = \beta' = 0$ implies $T_o = T_b$, so that the results can be shown vs. T_b in Figure 1.

To obtain comparable results for h' and h, when the variation in physical properties is taken into account, individual values of h and h' were evaluated at the same bulk temperature and Reynolds number. The coefficient for the nonreacting system was evaluated from the $\beta = 0$ curve of N_{Nu_o} vs. N_{Re_o}, as illustrated in Figure 4. The h' values for the reacting gas at a chosen value of β' and T_o were read from the curves of $N'_{Nu'_o}$ vs. N_{Re_o}. It was then necessary to compute T_b from the known values of β', T_o, and t^+_b by means of

$$\beta' = \frac{1}{t^+_b}\left(1 - \frac{T_b}{T_o}\right) \ldots\ldots \qquad (24)$$

This relationship results from applying Equation (22) to a reacting system and choosing the temperature to be the bulk mean value. In this way, by employing curves of $N'_{Nu'_o}$ vs. N_{Re_o} similar to Figure 4, the coefficient h' could be determined at the same T_b and N_{Re_o} as used to evaluate h. The results are shown in Figure 5 as h'/h vs. T_b. In contrast to the other analogies the values of h'/h are functions of the wall temperature and Reynolds number. Curves for various wall temperatures are shown in Figure 5, but all the solid curves apply for a Reynolds number of 100,000. The dotted line represents the predicted values of h'/h for constant physical properties; that is $\beta' = 0$. It is apparent that the effect of physical property changes can be significant, particularly at high wall temperatures and low bulk temperatures, between which c'_p and k' can pass through a maximum value.

DISCUSSION OF RESULTS

Figure 1, representing the predictions of the analogies with constant physical properties, is interesting in two respects. First the simple Reynolds and Colburn analogies predict results which differ from the more realistic predictions of Deisslers analogy (for constant properties) by less than 15%. In fact Reynolds procedure agrees within 10% of Deisslers approach. For inert systems the Deissler analogy compares more favorably with experimental heat transfer data than the simpler analogies over a range of Prandtl numbers. However the agreement is not appreciably better for gases where the Prandtl number is low and relatively constant. Secondly it is observed that all three analogies predict the same value of h'/h at about 320°K. It is near this temperature that $N_{Pr} = N'_{Pr}$ for the nitrogen tetroxide-dioxide system, as indicated by the data in Table 1. The explanation for this may be seen by eliminating $\Delta H^2/2\,RT^2$ from Equations (12) and (13). The result is

$$\frac{k'}{k} = 1 + \frac{C_p\,\rho\,D}{k}\left(\frac{C'_p}{C_p} - 1\right)$$

$$= 1 + \frac{C_p\,\rho\,D}{k}\left(\frac{C'_p}{C_p} - 1\right) \qquad (25)$$

where $C_p\,\rho\,D/k$, the Lewis number, is also equal to the ratio N_{Pr}/N_{Sc}. If the ratio of the Prandtl to the Schmidt number is unity, Equation (25) shows that

$$k'/k = C'_p/C_p$$

and hence

$$N_{Pr} = N'_{Pr}.$$

If the Prandtl numbers for the inert and reacting systems are equal, all analogies for which Stanton number is a function of Reynolds and Prandtl numbers will give the same result, equivalent to that for Reynolds analogy. This is illustrated for the Colburn analogy by Equation (17). In general this situation will occur only at specific temperatures for a given system. Hence the assumption of the Lewis number equal to unity is not valid for analyzing reacting systems over a range of temperature.

The large differences between the solid and dotted curves in Figure 5 point out the importance of attempting to take into consideration the radial variation in properties in a reacting system. The simpler procedures of using average properties in Reynolds or Colburns analogies lead to approximate results. These approximations can probably be improved by empirical rules for evaluating average properties. However these rules may have to be changed from system to system, making it hazardous to make predictions.

The results for other Reynolds numbers are similar to those shown in Figure 5 for $Re_o = 100{,}000$, although the magnitude of h'/h is different, especially at larger values of β'. For example at $Re_o = 10{,}000$ the maximum value of $h'/h = 13.6$ at $T_o = 370$°K. and $\beta' = 0.02$.

ACKNOWLEDGMENT

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NOTATION

C_p = specific heat (frozen or nonreacting value)at constant pressure, cal./(g.) (°C.)
D = diffusivity of nitrogen dioxide in nitrogen tetroxide-dioxide reacting mixture, sq. cm./sec.
d = tube diameter, cm.
g_c = gravitational constant, cm./sec.^{2}
$\Delta H_{N_2O_4}$ = heat of dissociation of nitrogen tetroxide, cal./mole.
h = heat transfer coefficient for frozen (inert or nonreacting system), cal./(sec.) (sq.cm.) (°C.)
h' = heat transfer coefficient for the reacting system, cal./(sec). (sq.cm.) (°C.)
K = equilibrium constant
k = thermal conductivity (frozen or nonreacting value), cal./(sec.) (cm.) (°C.)
m, b = constants in Equation (18)
N = diffusion rate, g.moles/sq.cm.
q = radial rate of heat transfer toward center of tube, per unit area, cal./(sec.) (sq. cm.)
p = partial pressure = $x\pi$, atm.
r_o = tube radius, cm.
T = absolute temperature—°K.
u = time average fluid velocity parallel to tube axis, cm./sec.
x = mole fraction
y = distance measured from tube wall toward center, cm.

Greek Symbols

α = fraction of nitrogen tetroxide dissociated
ϵ = eddy diffusivity, sq.cm./sec.
μ = viscosity, g./(cm.) (sec.)
π = total pressure = 1 atm.
ρ = density, g./cc.
τ = shear stress in fluid, g.cm./(sec.)^2(sq.cm.)

Dimensionless Groups

β = heat transfer parameter for nonreacting system, $\dfrac{q_o(\tau_o/\rho_o)^{1/2}}{C_{p_o}\,\tau_o\,T_o\,g_c}$.
$\beta' = \dfrac{q_o(\tau_o/\rho_o)^{1/2}}{C'_{p_o}\,\tau_o\,T_o\,g_c}$
N_{Le} = Lewis number, $C_p\,\rho\,D/k$
N_{Nu} = Nusselt number, hd/k; $N'_{Nu'} = h'd/k'$
N_{Pr} = Prandtl number for nonreacting systems, $C_p\mu/k$; $N'_{Pr'} = C'_p\mu/k$
N_{Re} = Reynolds number, $d\,u\,\rho/\mu$
r^+_o = dimensionless tube radius,

$$\frac{(\tau_o/\rho_o)^{1/2}}{\mu_o/\rho_o}r_o$$

t^+ = dimensionless temperature for nonreacting system,

$$\frac{1}{\beta}\left(1-\frac{T}{T_o}\right)\ ;\ (t^+)' = \frac{1}{\beta'}\left(1-\frac{T}{T_o}\right)$$

u^+ = dimensionless velocity,

$$\frac{u}{(\tau_o/\rho_o)^{1/2}}$$

y^+ = dimensionless distance,

$$\frac{(\tau_o/\rho_o)^{1/2}}{\mu_o/\rho_o}y$$

Subscripts and Superscripts

b = subscript denoting bulk mean conditions

o = subscript denoting wall conditions

– = molal basis

= value in reacting system

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Thermodynamics of Solvent Selectivity in Extractive Distillation of Hydrocarbons

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The selectivity of a polar solvent is expressed in terms of an approximate theory of solutions. The theoretical results are insufficiently precise for the accurate prediction of activity coefficients, but the analysis shows that in the absence of chemical effects selectivity depends primarily on the difference in molar volumes of the hydrocarbons to be separated and on the polar energy density of the solvent. The effectiveness of a solvent is related to its polarity (which should be large) and to its molecular size (which should be small). In cases where chemical effects are important or where the molar volumes of the hydrocarbons to be separated are only slightly different, selectivity also depends on the relative ability of the hydrocarbons in acting as electron donors and on the ability of the solvent to act as an electron acceptor in forming acid-base complexes. The theoretical conclusions, which are based on modern thermodynamics and on the theory of intermolecular forces, are in agreement with experimental observations. The results obtained in this work provide theoretical criteria for the selection of an optimum solvent for a given separation and give semiquantitative explanations of solution phenomena related to extractive distillation.

Separation of hydrocarbon mixtures by extractive distillation has been practiced industrially for many years, even though there has been only limited understanding of the fundamental phase equilibria which form the thermodynamic basis of this operation. In general it is known that the addition of polar solvents to hydrocarbon mixtures results, for example, in increased volatilities of paraffins relative to naphthenes, olefins, and diolefins, and in increased volatilities of naphthenes relative to aromatics; therefore the addition of a polar solvent enables facile separation by distillation of certain mixtures which otherwise can only be separated with difficulty. However almost all thermodynamic work in this area has been confined to obtaining vapor-liquid equilibria for isolated systems, and very little has been written on the fundamental molecular physics which could explain how selectivity works. This paper discusses selectivity from the viewpoint of modern thermodynamics and intermolecular forces and aims to provide a molecular basis for explaining why some solvents are more selective than others. The theory of solutions is at present insufficiently advanced to provide an exact quantitative treatment with which to predict the desired activity coefficients. However recent theoretical work in solution thermodynamics and results of physicochemical studies in intermolecular forces can be utilized to give a semiquantitative picture of solution behavior, to provide useful criteria in selection of an optimum solvent for a given separation, and to supply a theoretical framework for the correlation of experimental data.