

# CALCULATION OF PRE-EXPONENTIAL TERM IN KINETIC RATE EXPRESSION

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The rate of a chemical reaction is commonly expressed as

$$R = k(T)f(c) \quad (1)$$

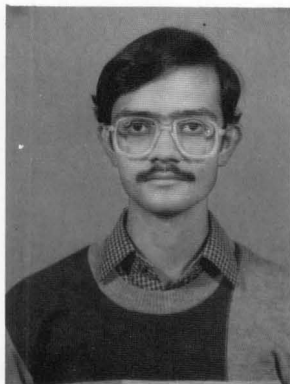
where  $k(T)$  is the rate constant and  $f(c)$  represents the effect of the concentration of all the relevant chemical species on the reaction rate. The effect of temperature on the rate constant is given by

$$k(T) = AT^m \exp\left[-\frac{E}{R_g T}\right] \quad (2)$$

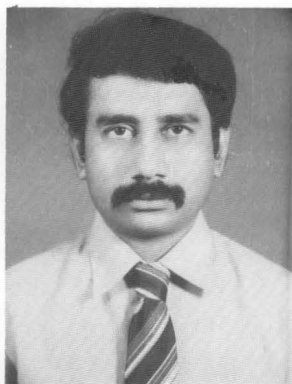
where

- $m = 1/2$  from the kinetic theory of gases
- $= 1$  from statistical mechanics
- $= 0$  from the Arrhenius relation

In the case of vapor phase reactions, it is customary and convenient to use partial pressures rather



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than the concentrations. For ideal gases, the molar concentration of an  $i^{\text{th}}$  species is related to its partial pressure by

$$C_i = \frac{P_i}{R_g T} \quad (3)$$

Substituting Eqs. (2) and (3) in Eq. (1)

$$R = A(T) \exp\left[\frac{-E}{R_g T}\right] f(p) \quad (4)$$

where the pre-exponent is now a function of temperature. However, it is generally assumed that the effect of temperature in  $A(T)$  is dwarfed by that in the exponential term, and hence the reaction rate can simply be expressed as

$$R = A' \exp\left[\frac{-E'}{R_g T}\right] f(p) \quad (5)$$

where the pre-exponent  $A'$ , just like  $A$  in Eq. (2), is treated to be constant. It was in fact shown by Smith [1] that, for a simple first order reaction, the use of Eq. (5) instead of Eq. (4) would lead to insignificant error.

However, the validity of the above assumption depends on the values of the activation energy, the reaction order and the temperature range. The purpose of this article is to show that significant errors may result, under certain conditions, if Eq. (5) is used instead of Eq. (4) in the estimation of kinetic parameters from the experimental data to be used in the reactor design.

## PROBLEM STATEMENT

Let us consider an  $n^{\text{th}}$  order reaction such that

$$f(C) = C_i^n \quad (6)$$

Substituting Eq. (6) in Eqs. (4) and (5), respectively,

$$R = k(T)p_i^n; \quad k(T) = \frac{A}{R_g^n} T^{m-n} \exp\left[\frac{-E}{R_g T}\right] \quad (7)$$

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and

$$R = k'(T)p_i^n; \quad k'(T) = A' \exp\left[\frac{-E'}{R_g T}\right] \quad (8)$$

By nondimensionalising the temperature with a reference temperature  $T_o$ , the rate constants in Eqs. (7) and (8) can be rewritten as

$$k(t) = k_o t^{m-n} \exp\left[-e\left(\frac{1}{t} - 1\right)\right] \quad (9)$$

and

$$k'(t) = k'_o \exp\left[-e'\left(\frac{1}{t} - 1\right)\right] \quad (10)$$

where

$$t = \frac{T}{T_o}; \quad e = \frac{E}{R_g T_o}; \quad e' = \frac{E'}{R_g T_o}$$

$$k_o \frac{A}{R_g^n} T_o^{m-n} \exp[-e] \quad \text{and} \quad k'_o = A' \exp[-e']$$

Typically, using the experimental isothermal rate versus partial pressure data, the rate constants at different temperatures are calculated. In turn, these rate constant versus temperature data are used for the estimation of the activation energy and the pre-exponential constant. Obviously, the value of the activation energy (and so the pre-exponential constant) will be different depending on whether Eq. (9) or Eq. (10) is used. Also, one can expect the difference between the "real" and "apparent" activation energies, *i.e.*

( $e - e'$ ), to increase with the reaction order. Moreover, this difference should be expected to vary with the temperature range. It can also be seen that the difference between  $e$  and  $e'$  will not depend on the value of  $e$ . These points will be illustrated next.

### PARAMETRIC ESTIMATION

As an easier alternative to obtaining the best fitting values of  $e$  and  $e'$  for a given set of rate constant versus temperature data, we adopt the following procedure. First, specific values are assigned to  $n$  (1 to 3) and  $e$  (5 to 30).  $k_o$  is conveniently taken to be unity and  $m$  to be zero. Then, using Eq. (9),  $k$  versus  $t$  data are generated at several discrete points over a temperature range of  $1.0 \leq t \leq 2.0$ . Finally, using the expression in Eq. (10), the best fitting values of  $k'_o$  and  $e'$  for the above data are computed by standard numerical techniques.

### DISCUSSION

As seen from the results summarized in Table 1, the difference between  $e$  and  $e'$  increases with the

TABLE 1 Errors in Rate Constant				
Reaction order, $n$	Activation energy (dimensionless)		% error in activation energy $= 100\left(\frac{e-e'}{e}\right)$	Range of % error in rate constant $= 100\left(\frac{k'-k}{k}\right)$
	$e$	$e'$		
1	5.0	3.60	-28.0%	-2.2 to +4.2%
	10.0	8.60	-14.0%	
	20.0	18.60	-7.0%	
	30.0	28.60	-4.7%	
2	5.0	2.20	-56.0%	-4.4 to +8.6%
	10.0	7.20	-28.0%	
	20.0	17.20	-14.0%	
	30.0	27.20	-9.3%	
3	5.0	0.80	-84.0%	-6.5. to 13.1%
	10.0	5.80	-42.0%	
	20.0	15.80	-21.0%	
	30.0	25.80	-14.0%	

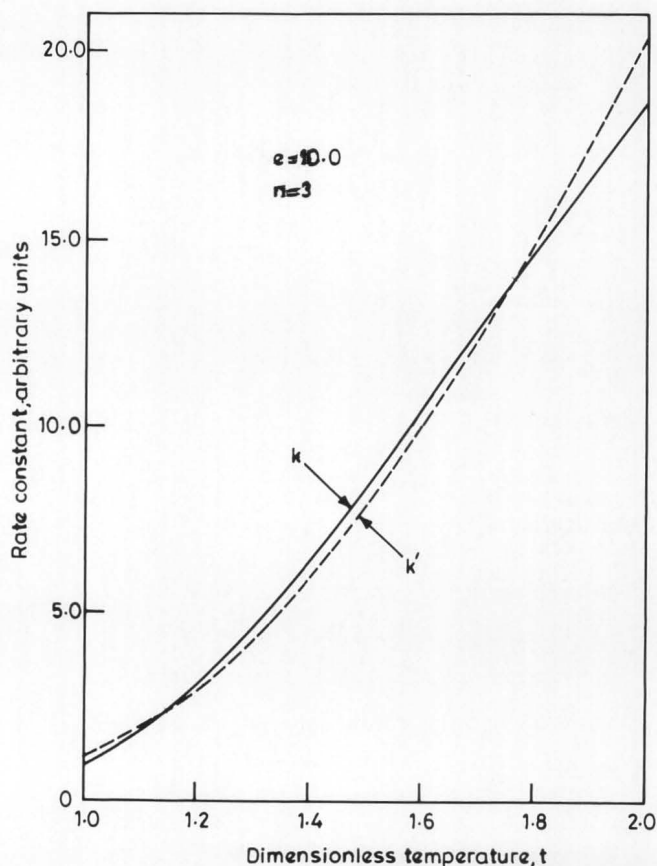


FIGURE 1. Real and apparent rate constants versus temperature.

value of  $n$ ; however, this difference remains unchanged with the variation of the  $e$  value. Consequently, the percentage error in the apparent activation energy is the highest for the highest reaction order and the lowest (real) activation energy. Another kind of error also appears as a result of forcing an approximate function  $k'(t)$  to represent the "real"  $k$  vs.  $t$  data. As shown in Figure 1, when  $k'$  is plotted against  $t$  (using, of course, the computed values of  $k_0'$  and  $e'$ ), this curve does not conform accurately with the real  $k$  vs.  $t$  curve. The deviation of  $k'$  from  $k$  increases, as shown in Table 1, with the reaction order. This deviation is also a function of the temperature range. For example, the deviation of  $k'$  from  $k$  will be within  $\pm 2\%$  for  $1.0 \leq t \leq 1.25$  as against  $\pm 13\%$  for  $1.0 \leq t \leq 2.0$  for a third order reaction.

If the value of  $m$  is taken to be unity instead of

zero in Eq. (9), the errors will be reduced by one order. Also, the errors shown in Table 1 are likely to be somewhat smaller if instead the values of  $e$  and  $e'$  are computed using the actual experimental data, which are generally error-ridden.

Finally, let us see what happens when  $k'(t)$  instead of the real  $k(t)$  is used in the reactor design equations. As an illustration, two consecutive exothermic reactions are assumed to be taking place in an ideal nonadiabatic plug flow reactor. The design equations and specifications along with the results are shown in Table 2. It is seen that the use of Eq. (10) instead of Eq. (9) in the design equations leads to significant errors in the prediction of the reactor performance. It should, however, be noted that the conditions in the example are chosen so as to magnify the possible errors.

## REFERENCE

1. Smith, J. M., *Chemical Engineering Kinetics*, McGraw-Hill, New York, 1981, 48-51.

**TABLE 2**  
Reactor Specifications and Performance

### Mass Balance:

$$\frac{dx}{dz} = a_1 \exp\left[-e_1\left(\frac{1}{t}-1\right)\right]\left[\frac{1-x}{t}\right]^{n_1} + a_2 \exp\left[-e_2\left(\frac{1}{t}-1\right)\right]\left[\frac{1-x}{t}\right]^{n_2} \quad (11)$$

or

$$= a'_1 \exp\left[-e'_1\left(\frac{1}{t}-1\right)\right][1-x]^{n_1} + a'_2 \exp\left[-e'_2\left(\frac{1}{t}-1\right)\right][1-x]^{n_2} \quad (12)$$

### Heat Balance:

$$\frac{dt}{dz} = a_3 \frac{dx}{dz} - a_4 (t - t_w) \quad (13)$$

### Specifications:

$$\begin{aligned} n_1 &= 3; & n_2 &= 2; & e_1 &= 10.0; \\ e_2 &= 20.0; & e'_1 &= 5.80; & e'_2 &= 17.20; \\ a_1 &= 0.0600; & a_2 &= 0.0400; & a_3 &= 11000; \\ a_4 &= 0.0500; & a'_1 &= 0.0689; & a'_2 &= 0.0434; \\ t_w &= 0.8; & \text{Inlet conditions: } & x = 0, & t &= 1.0 \end{aligned}$$

### Results:

	Exit Conversion, $x$	Exit Temperature, $t$
Using Eqs. (11) and (13)	27.6	1.289
Using Eqs. (12) and (13)	34.9	1.368

## NOMENCLATURE

A	= Pre-exponential factor of the rate constant
$a_1$ - $a_4$	= reactor parameters in Eqs. (11)-(13)
C	= molar concentration
E	= activation energy
e	= dimensionless activation energy
f	= concentration (partial pressure) dependence function
k	= reaction rate constant
m	= a constant in Eq.(2)
$n, n_1, n_2$	= reaction order
p	= partial pressure
R	= reaction rate
$R_g$	= gas constant
T	= temperature
t	= dimensionless temperature
x	= fractional conversion of the reactant
z	= dimensionless length coordinate

## Subscripts

i	= $i^{\text{th}}$ chemical species
o	= at the reference temperature
w	= at the reactor wall

## Superscripts

'	= partial pressure based values □
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