RESEARCH NOTE

SOFTWARE FOR KINETIC PROCESS SIMULATION

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Abstract The relationship between velocity of chemical reactions with activities or concentrations of their reactants, temperature and pressure and the mechanisms through which the reactions proceed are of interest to many scientists and engineers. The purpose of this article is to introduce a computer software that is developed for calculation, classification and collection of such data. The application of this software to the homogeneous and heterogeneous processes occurring in porous and non-porous media of flat, cylindrical or spherical geometry is tested. The software is capable of assisting the professional process design engineers as well as the general process kinetic investigators.

چکیده   رابطۀ بین سرعت یک واکنش شیمیایی با اکتیویته یا غلظت واکنشگرها، دما و فشار و مکانیزمی که واکنش از طریق آن پیش می‌رود مورد توجه و علاقه پژوهشگران و مهندسین بسیاری قرار گرفته است. هدف این مقاله معرفی نرم افزاری است که برای محاسبه، طبقه بندی و جمع آوری این نوع اطلاعات ساخته شده است. این نرم افزار در رابطه با فرایندهای همگن و غیر همگن در محیطهای متخلخل و غیر متخلخل دارای اشکال هندسی مستوی، استوانه ای و کروی کاربرد دارد. نرم افزار قادر است وظیفه طراحی فرایند در سطح حرفه ای را به عهده دارند و نیز پژوهشگرانی که در باره فرایندهای عمومی سیتیک تحقیق می‌کنند را یاری نماید.

1. INTRODUCTION

Looking after kinetic data is a fundamental task in any research scheme proposed to develop a modified material, a new process or an innovative technology. Present literature indicates, however, vast dispersion and scarcity of the kinetic information, which because of the differences in vocabulary and method of approach can hardly be integrated. Standardization of these data may be helpful to future advancements in the field of materials technology.

Two crucial pieces of information required in any dynamic materials system design and control are the rate and the mechanism through which a reaction proceeds. Despite accessibility of a number of thermodynamic information sources [1-8], there is no comprehensive collection as yet made available on the kinetics of chemical processes. While many flow-sheet modeling programs are using thermodynamic information for simulation of unit processes and unit operations [9-14], the inability of these simulators to incorporate the rate models into their energy and mass balance calculations is basically due to the complexity and vagueness of such information.

Kinetic calculations usually involve determination of an overall rate-constant that can be divided into several individual constants and an order of reaction that can be attributed to an elementary or a complex, a homogeneous or a heterogeneous and a catalytic or a non-catalytic reaction. The procedure is of interest. It consists of insertion of the

experimental data into a number of pre-specified algorithms and evaluation of the fitness of the results. The application of a mathematical technique in these calculations is usually inevitable [15-18].

Selection and application of the appropriate equations from a large set of possible relationships [19-26] is not a simple procedure. The traditional way of doing this is to examine the experimental data with several possible equations by trial-and-error technique. This is a two-stage procedure: first to find the concentration dependency at a specified temperature; next to repeat for finding the influence of temperature. Doing this in the traditional way is inevitably long, tedious and time-consuming. The curve-fitting techniques must be used in most cases. The accuracy of the data still remains uncertain.

The usual way of insertion of the empirical data into the rate models is endlessly long. A standard procedure does not exist to help the investigator to reach a non-sophisticated conclusion. Too many possibilities must be checked. More than one mechanism may be found. Different models may match with the data. More than one path may exist for the process. Too much scatter in the empirical data may make the investigator unable to assess the strength and validity of the result.

A comprehensive kinetic study should include both macro-models for determination of parameters of the rate equation and micro-models for determination of the process steps. Computer software that can do both is not practically available. Two programs that make the rate process calculations are CRS [27] and SMAK [28]. CRS simulates the kinetics of chemical reactions from prior experimental data. SMAK is software for calculating the rate of slag-metal-gas reactions in smelting and refining systems. Both programs need, however, further developments to become able to calculate the rate process coefficients of the complicated kinetic systems of interest [10].

The purpose of this paper is to describe the capability and merits of the personal computer software KPS (Kinetic Process Simulation) which is developed to calculate and store the rate process coefficients from both prior experimental data and the available literature. KPS is a modification of the previous program called CRS [27] and is capable to determine the overall rate equation,

the temperature effect and the mechanism through which an unknown reaction proceeds to the end. It covers, therefore, major areas of both macro-model and micro-model kinetic simulation. A database program called KPS-DB (Kinetic Process Simulation Data-Base) is also attached to KPS to hold the rate data of interest. At present KPS-DB contains some 200 reactions of mostly metallurgical applications.

2. MATHEMATICAL PROCEDURE

Figure 1 shows the flow-chart of the integral method. The mathematical algorithm is based on obtaining the minimum coefficient of variation of k. The procedure is to calculate the rate constant k for all values of the reaction order n being raised iteratively within the limits specified by the user. For the simplest case of an isolated reactant, Equation 1 is used to calculate the rate constant of the reaction:

$$n \neq 1 \qquad k = \frac{1}{t(n-1)C_{A0}^{n-1}} \left[\frac{1}{(1-X_A)^{n-1}} - 1 \right]$$

$$n = 1 \qquad k = \frac{1}{t} \ln \frac{1}{1-X_A} \qquad (1)$$

If the fit does not prove satisfactory, the procedure can be repeated with another equation.

The user must notice the importance of assigning a proper range for n. If the range is too narrow, a false result may be obtained due to the existence of local minima in the coefficient of variation of k versus reaction order (Figure 2). The results are generally not too sensitive to the difference in the reaction order, δn. However decreasing the value of δn does increase the accuracy of the result.

In the differential method, two kinds of reaction order, n_t and n_C, are determined. The former, n_t, is based on the experimental evaluation of the rate of reaction for a single initial concentration at different times. This usually corresponds to the order obtained through the application of the integral method to the time-concentration data. The latter, n_C, is based on the experimental evaluation of the rate of reaction at different initial concentrations.

S

n=LL

n=1

Y

$$k = \frac{\sum k_i}{\sum i}$$

$$k = \frac{1}{t} \ln \frac{1}{1 - X_A}$$

N

$$k = \frac{\sum k_i}{\sum i}$$

$$k = \frac{1}{t\,(n-1)C_{A0}^{\,n-1}} \left[\frac{1}{(1 - X_A)^{n-1}} - 1 \right]$$

CV

n=LL

Y

N

CF > CV

Y

N

CF = CV
n = n
k = k

$$n = n + \delta n$$

n > U.L.

Y

N

n

k

E
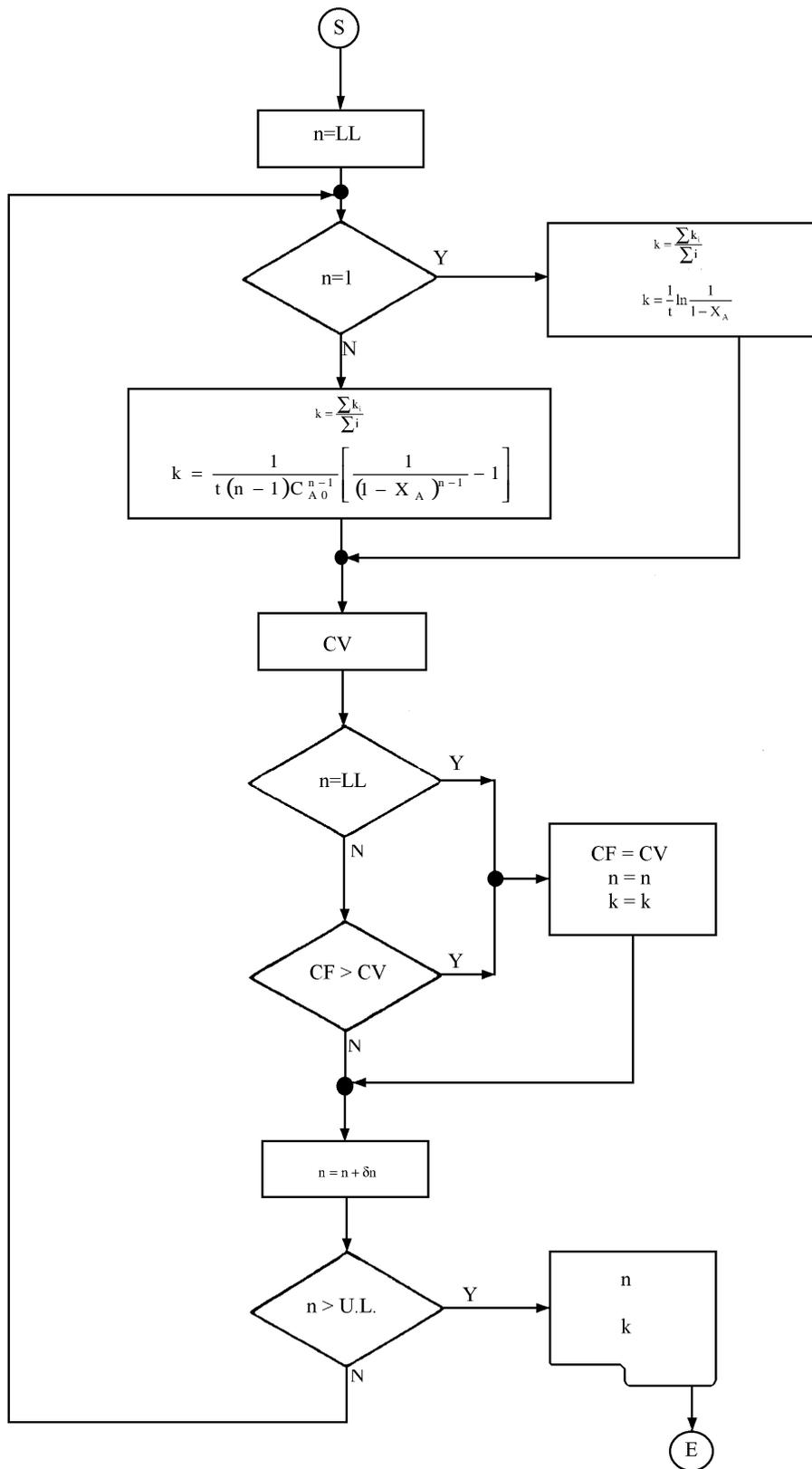
Figure 1. Flow-chart of the integral method.
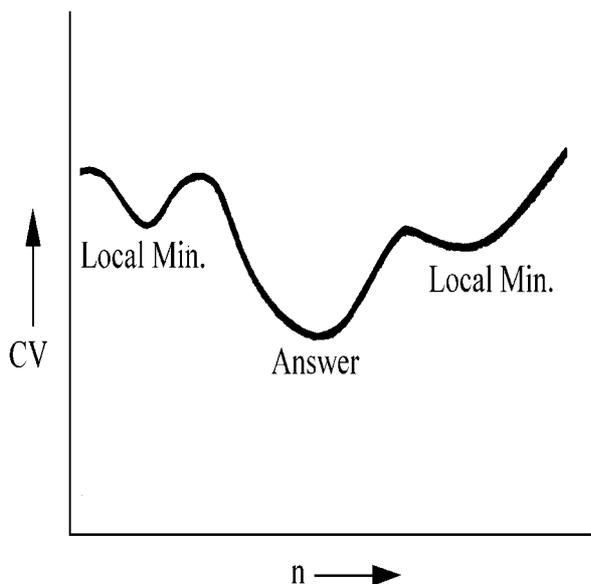
Figure 2. Local minima in the coefficient of variation of k.

A plot of $\ln(-dC/dt)$ vs. $\ln C$ would simply give the values of n and k (Figure 3). The accuracy of the results depends on the mathematical technique used for evaluation of the rate of the reaction from concentration versus time curves and the number of the data-points being empirically available. At this stage, the method of Regression Analysis is used to find the best matching line with the most appropriate slope and intercept.

The rate of a chemical reaction is also related to temperature. The influence of temperature is evaluated by application of the Arrhenius Law. Linear Regression Analysis is used to determine the slope and the intercept of the leading curve.

Work is underway to add a subroutine for determination of complex mechanisms for those reactions whose orders are different from their molecularity or stoichiometric factors. Examples of ordinary complex reactions are given in Table 1. The

TABLE 1. Micro-Models for Homogeneous Complex Reactions [19,20].

Overall Reaction	Mechanism	Rate Equation
$2A_2B \rightarrow 2AB + A_2$	$A_2B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB + A^+$ $A_2B + A^+ \underset{k_4}{\overset{k_3}{\rightleftarrows}} AB + A_2$	$\dfrac{dC_{A_2}}{dt} = \dfrac{k_1 k_3 C_{AB}^2 - k_2 k_4 C_{AB}^2 C_{A_2}}{k_2 C_{AB} + k_3 C_{A_2B}}$
$A + B \rightarrow C$	$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} A^+$ $A + B \underset{k_4}{\overset{k_3}{\rightleftarrows}} C^+$	$\dfrac{dC_C}{dt} = \dfrac{k_1 k_3 C_A C_B^2 - k_2 k_4 C_C}{k_2 + k_3 C_B}$
$2A + B \rightarrow A_2B$	$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB^+$ $AB^+ + A \underset{k_4}{\overset{k_3}{\rightleftarrows}} A_2B$	$\dfrac{dC_{A_2B}}{dt} = \dfrac{k_1 k_3 C_A^2 C_B - k_2 k_4 C_{A_2B}}{k_2 + k_3 C_A}$
$A_2 + B_2 \rightarrow 2AB$	$A_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2A$ $A + B_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} AB + B$ $A_2 + B \overset{k_5}{\rightarrow} AB + A$	$\dfrac{dC_{AB}}{dt} = \dfrac{2k_3 C_{B_2} \sqrt{\dfrac{k_1}{k_2} C_{A_2}}}{1 + \dfrac{k_4}{k_5} \dfrac{C_{AB}}{C_{A_2}}}$
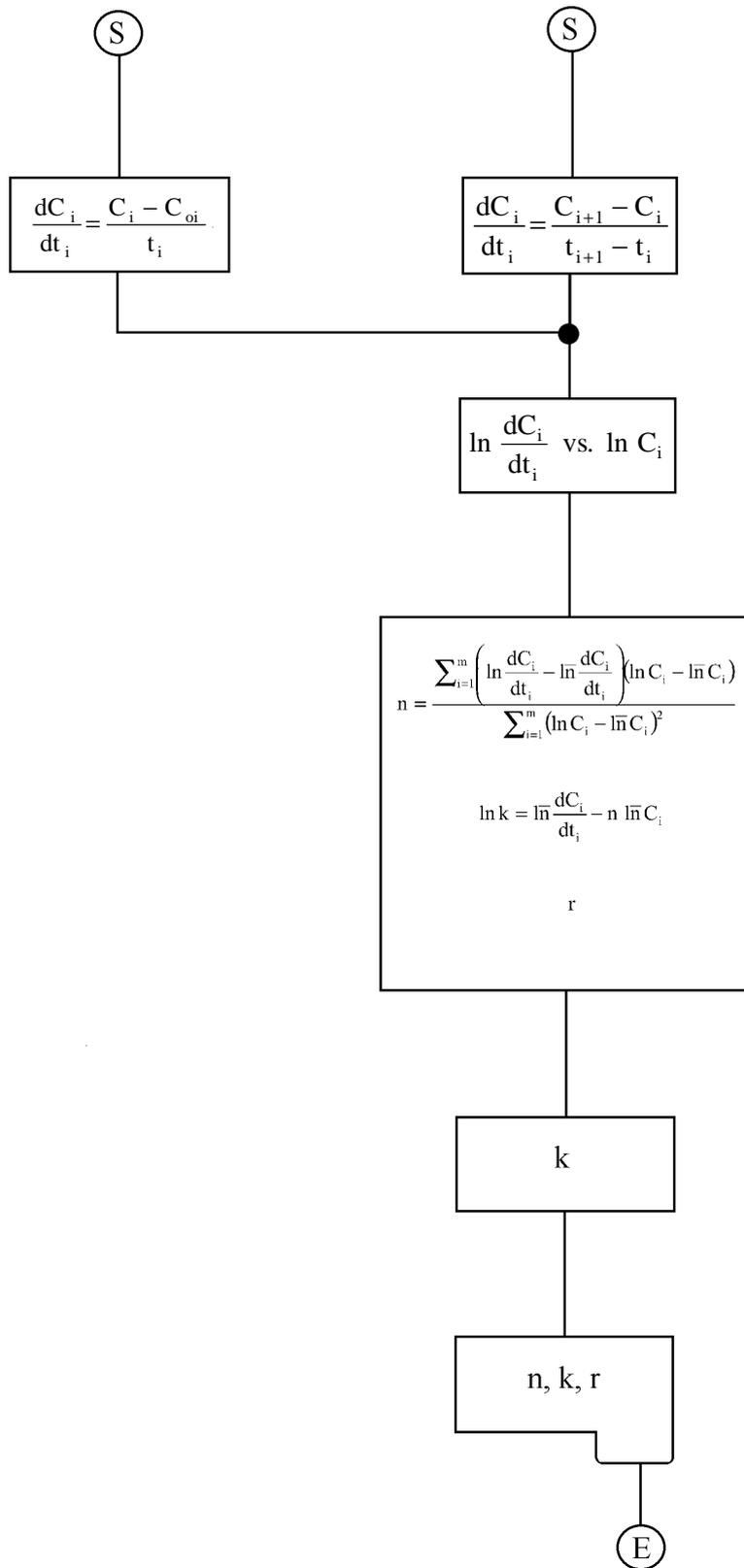
Figure 3. Flow-chart of the differential method.

TABLE 2. Isothermal Heterogeneous Models [21-25] for First Order Chemical Reaction Combined with Internal, External and Pore Diffusion.

Particle	Specific Parameter	Dimensionless Conversion Time
Non-Porous, Constant-Size	---	$t^* = g_{F_g}(X) + \phi_g^2 . P_{F_g}(X) + \phi_g^2 \dfrac{2}{Sh^*} q_{F_g}(X)$
Non-Porous, Variable-Size	$Z = \dfrac{\rho_B d\, M_D}{\rho_D b\, M_B}$	$t^* = g_{F_g}(X) + \phi_g^2 . P_{F_g}(X) + \phi_g^2 \dfrac{2}{Sh^*} q_{F_g}(X)$
Porous, with Constant- or Variable-Size Grains	$\phi_P^2 = \dfrac{(1-\varepsilon)kF_P}{2D_e}\left(\dfrac{V_P}{A_P}\right)^2 \dfrac{A_g}{F_g V_g}$	$t^* = g_{F_g}(X) + \phi_g^2 . P_{F_g}(X) + \phi_p^2 . P_{F_P}(X) + \phi_P^2 . \dfrac{2}{Sh^*} q_{F_P}(X)$

A. Constant-Size Grain

Geometry	Disc (Fg=1)	Cylinder (Fg=2)	Sphere (Fg=3)
$g_{F_g}(X)$	X	$1 - (1-X)^{\frac{1}{2}}$	$1 - (1-X)^{\frac{1}{3}}$
$p_{F_g}(X)$	X^2	$X + (1-X)\ln(1-X)$	$1 + 2(1-X) - 3(1-X)^{\frac{2}{3}}$
$q_{F_g}(X)$	X	X	X
ϕ_g^2	$\dfrac{kV_g}{2D_g A_g}$	$\dfrac{kV_g}{2D_g A_g}$	$\dfrac{kV_g}{2D_g A_g}$
Sh^*	$\dfrac{h_D l_0}{D_e}$	$\dfrac{h_D r_0}{D_e}$	$\dfrac{h_D r_0}{D_e}$

B. Variable-Size Grain

Geometry	Disc (Fg=1)	Cylinder (Fg=2)	Sphere (Fg=3)
$g_{F_g}(X)$	X	$1 - (1-X)^{\frac{1}{2}}$	$1 - (1-X)^{\frac{1}{3}}$
$p_{F_g}(X)$	X^2	U_1	U_3
$q_{F_g}(X)$	X	U_2	U_4
ϕ_g^2	$\dfrac{kl_0}{2D_g} \cdot Z$	$\dfrac{kl_0}{4D_g} \cdot \left[\dfrac{-Z\ln Z}{1-Z}\right]$	$\dfrac{kl_0}{2D_g} \cdot \left[\dfrac{Z^{\frac{2}{3}} - Z}{1-Z}\right]$
Sh^*	$\dfrac{h_D l_0}{D_e} \cdot Z$	$\dfrac{h_D l_0}{D_e} \cdot \left[\dfrac{-Z\ln Z}{2(1-Z)^{1/2}}\right]$	$\dfrac{h_D l_0}{D_e} \cdot \left[\dfrac{Z^{\frac{2}{3}} - Z}{1-Z^{\frac{1}{3}}}\right]$

$$U_1 = \frac{(1-Z)(1-X)\ln(1-X)}{-Z\ln Z} - \frac{[(1-Z)(1-X)+Z]\ln[(1-Z)(1-X)+Z]}{-Z\ln Z} \; ; U_2 = \frac{1 - [(1-Z)(1-X)+Z]^{1/2}}{1 - Z^{\frac{1}{2}}}$$

$$U_3 = \frac{Z + (1-Z)(1-X)^{\frac{2}{3}} - [Z+(1-Z)(1-X)]^{\frac{2}{3}}}{Z - Z^{\frac{2}{3}}} \; ; \qquad\qquad U_4 = \frac{1 - [(1-Z)(1-X)+Z]^{\frac{1}{3}}}{1 - Z^{\frac{1}{3}}}$$

TABLE 3. Sample-Reactions from KPS-DB.

Reaction	Mechanism	Speed[*]	Rate Equation
Aqueous			
$2Cr^{2+}_{(aq)} + Ti^{3+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + Ti^{+}_{(aq)}$	$Cr^{2+}_{(aq)} + Ti^{3+}_{(aq)} \rightarrow Cr^{3+}_{(aq)} + Ti^{2+}_{(aq)}$	s	$-\dfrac{dC_{Ti^{3+}}}{dt} = kC_{Cr^{2+}}C_{Ti^{3+}}$
	$Cr^{2+}_{(aq)} + Ti^{2+}_{(aq)} \rightarrow Cr^{3+}_{(aq)} + Ti^{+}_{(aq)}$	f	
$H_3AsO_{4(aq)} + SO_{2(aq)} + H_2O_{(aq)}$ $\rightarrow H_3AsO_{4(aq)} + H^+{(aq)} +$ $HSO^-_{4(aq)}$	$H_3AsO_{4(aq)} + SO_{2(aq)} \rightarrow$ $SO_{3(aq)} + H_3AsO_{3(aq)}$	s	$-\dfrac{dC_{H_3AsO_4}}{dt} = kC^2_{SO_2}C_{H_3AsO_4}$
	$SO_{3(aq)} + H_2O_{(aq)} \rightarrow H^+{(aq)} + HSO^-_{4(aq)}$	f	$n = 1.04 \pm 0.13$
Gaseous			
$CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$	$Cl_{2(g)} \underset{\leftarrow}{\overset{\rightarrow}{}} 2Cl_{(g)}$	f	$-\dfrac{dC_{COCl_2}}{dt} = kC^{3/2}_{Cl_2}C_{CO}$
	$CO_{(g)} + Cl_{(g)} \underset{\leftarrow}{\overset{\rightarrow}{}} COCl_{(g)}$	f	
	$COCl_{(g)} + Cl_{2(g)} \underset{\leftarrow}{\overset{\rightarrow}{}} COCl_{2(g)} + Cl_{(g)}$	s	
Liquid-Gas			
$\underline{C}_{(l)} + CO_{2(g)} \rightarrow 2CO_{(g)}$	$CO_{2(g)} \rightarrow CO_{2(ad)}$	s	$-\dfrac{dC_C}{dt} = kP_{CO_2}$
	$CO_{2(ad)} \underset{\leftarrow}{\overset{\rightarrow}{}} O_{(ad)} + CO_{(ad)}$	f	
	$\underline{C}_{(l)} \underset{\leftarrow}{\overset{\rightarrow}{}} C_{(ad)}$	f	$\ln k = -\dfrac{11.700}{T} - 0.48$
	$C_{(ad)} + O_{(ad)} \underset{\leftarrow}{\overset{\rightarrow}{}} CO_{(ad)}$	f	$k: \left(\dfrac{mol}{cm^2 \cdot s \cdot atm}\right)$
	$2CO_{(ad)} \underset{\leftarrow}{\overset{\rightarrow}{}} 2CO_{(g)}$	f	
Solid-Gas			
$ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2(g)$	Diffusion of CO through the external layer of gas	c	$-\dfrac{dn_{ZnO}}{dt} = -\dfrac{P \cdot X_{CO}}{RT\left[\dfrac{1}{k} + \dfrac{1}{h_D}(1 + X_{CO})\right]}$
	$CO_{(g)} \rightarrow CO_{(ad)}$	c	
	$CO_{(ad)} + ZnO_{(s)} \rightarrow Zn_{(g)} + CO_{2(g)}$	c	

* Relative speeds: f (fast), c (comparable) and s (slow)

application of the integral or the differential method to the empirical data can help the user to determine whether the reaction is elementary or complex.

The experimental data are incorporated into the micro-models to determine the possible elementary steps involved in the overall process. For heterogeneous gas-solid reactions, a micro-model is associated at this stage with a simple geometric (flat, cylindrical or spherical) rate equation for both non-porous and porous reacting particles, which include simple geometric grains (Table 2). Application of the models to the case of particles immersed in a liquid environment is also feasible.

Three essential assumptions of the heterogeneous models are: (1) shrinking core model with a first-order chemical reaction, (2) nonparallel consecutive kinetic steps and (3) convective mass transfer in the gas phase and (4) diffusive mass transfer in porous and/or nonporous phases of the system. The time for the total conversion of the solid reactant and its coefficient of variation are determined from incorporation of the empirical data into the appropriate rate equations. A

TABLE 4. The Batch Reactor Data of Hellin and Jungers [20] on the Reaction of Sulfuric Acid with Diethylsulfate in Aqueous Solution at 295.9°K.

Time (Minutes)	$C_{H_2SO_4} = C_{(C_2H_5)_2SO_4}$ (mole/liter)	Fractional Conversion
0	5.500	0
41	4.910	0.10727
48	4.810	0.12545
55	4.685	0.14818
75	4.380	0.20364
96	4.125	0.25000
127	3.845	0.30091
146	3.620	0.34182
162	3.595	0.34636
180	3.445	0.37364
194	3.345	0.39182
212	3.275	0.40455
267	3.070	0.44182
318	2.925	0.46818
368	2.840	0.48364
379	2.825	0.48636
410	2.790	0.49273

modification of the least square technique developed for all functional coefficients being positive is used to find the best fit of the data.

3. KPS DATA BASE

KPS-DB is developed for compilation of the kinetic information on the mechanisms of the complex reactions. The state-of-the-art of the reactions of interest are systematically determined through a careful search of the literature and compiled into the database. The program can help the user to sort, modify, save, search and recover the micro- and macro-model information on the rate of the reactions. The database includes some reactions of practical interest at present. Table 3 represents sample-reactions depicted from this database.

Because of the nature of the rate data, the task

of incorporation of the available data into KPS-DB is in its infancy. KPS and KPS-DB are, however, available to individual researchers for producing,

TABLE 5. Rate Constants of Reaction 2. The Figures are Obtained from the Data Given in Reference 29.

Temperature (ºK)	Rate Constant ($10^5 \, s^{-1}$)
868	1.48
903	2.17
933	2.92
963	4.21
993	5.57
1023	7.79
1053	9.79
1083	11.51

TABLE 6. Experimental Data on Direct Reduction of Spherical MoS$_2$ Pellets with Hydrogen at 1173 °K [30].

time (min.)	Concentration (mass % S)	Fractional Conversion
0	37.30	0
4	29.09	0.22
8	21.63	0.42
12	17.90	0.52
16	12.68	0.66
20	10.82	0.71
24	8.21	0.78
28	7.46	0.80
32	7.09	0.81
40	6.71	0.82
48	6.34	0.83
56	5.97	0.84
60	5.60	0.85

entering and recovering the rate data for specific reactions of immediate interest in a standardized way.

4. REAL-DATA APPLICATIONS

MKS consults a set of homogeneous and heterogeneous rate equations (Tables 1 and 2) for quantitative examination of the experimental data. Examples are given as follows. The purpose of the examples is only to see how the program works. Elaboration on the usefulness and merits of each specific example may require much further detail that can be discussed elsewhere.

Example 1. Formation of C$_2$H$_5$HS0$_4$ What is the overall order and the rate constant of the following reaction?

$$H_2SO_4(aq) + (C_2H_5)_2SO_4(aq) \rightarrow$$
$$2C_2H_5HSO_4(aq)$$
$$(2)$$
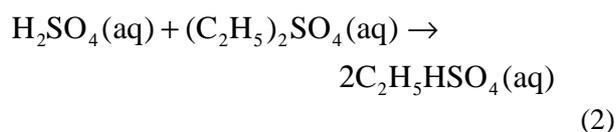
KPS can evaluate, from the experimental data,

the rate constant and the overall order of the reaction both rapidly and precisely. Running the integral command of the program yields, for example, an overall order of 2.64 with a rate constant of 2.18×10^{-4} for the data given in Table 4. More information on the relative concentrations of the reactants is required to determine the contributions to the overall order of each individual reactant.

Example 2. Reduction of MoO$_2$ with Hydrogen Arrhenius' Law calculations show an activation energy of 9300R and a frequency factor of 0.652 s^{-1} for the following reaction:

$$MoO_2(s) + 2H_2(g) \rightarrow Mo(s) + 2H_2O(g) \qquad (3)$$

The rate-data used in calculations is given in Table 5.

Example 3. Direct Reduction of MoS$_2$ with Hydrogen KPS can evaluate the rate controlling mechanism of the multi-step fluid-solid processes from the experimental result. An example is the

experimental data illustrated in Figure 4. Based on these data, KPS finds that the internal diffusion of gas in the solid grains can control the reduction rate. This finding is consistent with those analytically obtained from the data of Mankhand and Prasad [31] and Sinadinovic and Durkovic [32].

5. COMPUTER SYSTEM REQUIREMENT

Any computer supporting MS DOS version 3.3 and over can be used to run KPS and KPS-DB. A math co-processor is not required but is recommended. HP and LQ compatible printers can be attached to the system to print the graphs produced by KPS. Large computer memory is recommended for storing data-files and kinetic mechanism database.

6. SUMMARY

Since the traditional way of doing kinetic calculations is generally time-consuming and tedious, KPS is developed to save the investigators' valuable time and effort. KPS is interactive software with context-sensitive help facility that less expert and the infrequent users can also get benefit of it. The appearance of the program is much like that of a spreadsheet. The software is capable of storing a nearly unlimited (10^9) number of data points into an unlimited number of data-files. The empirical data can be gathered from the literature or supplied by the user.

Empirically determined activities, partial pressures, chemical compositions or conversion fractions can be utilized as the raw data. With the help of KPS, an overall order and a rate constant will be obtained for every homogeneous or heterogeneous reaction. These calculations can be done by application of either or both of the integral or the differential method. The former is capable of finding a relatively precise answer while the latter is an expeditious method for obtaining a first-glance roughly estimated result.

The integral method yields an overall order and a rate constant irrespective of the mechanism by which the reaction proceeds. The differential method yields, on the other hand, two sets of rate data. The first set corresponds to a with-respect-to-time (i.e.

apparent) order (n_t) which is produced from the slopes of concentration vs. time curves at different times, the latter has a with-respect-to-concentration (i.e. true) order (n_C) which is determined from the same-time slopes of the curves with different initial concentrations. The method of Regression Analysis is used to find the best fitted line with the most appropriate slope and intercept.

The scope of the program is to perform calculations on isolated reactants each at a time. The individual contributions can then be combined to yield the overall rate expression with respectable reactant orders. A rate equation is determined for any homogeneous reaction whether elementary or complex. If the stoichiometric coefficients are not the same as the orders obtained, a computerized search can be done for obtaining the most appropriate mechanism consistent with the rate equation and the stoichiometry of the reaction.

The effect of temperature on the rate of reactions is determined through the application of the Arrhenius' Law of the activated states. The present version is able to evaluate the frequency factor and the activation energy of the reaction. The frequency factor and the activation energy can then be utilized for further assessment of the mechanism of the rate process.

The program can consult a set of complex rate equations (Table 2) for quantitative examination of the experimental data. The well-known heterogeneous gas-solid systems of specific geometric shapes are tested to find the most appropriate models describing the heterogeneous rate equations of interest. MKS determines the total reaction time and the most effective controlling rate step.

The kinetic data produced by the individual researchers as well as those obtained through careful study of the literature can be standardized and compiled into the data-base program KPS-DB. The program critically tests some important features of the macro- or the micro-models associated with the homogeneous and/or heterogeneous processes of engineering applications.

8. NOMENCLATURE

A   frequency factor
A_g area of a grain
A_p area of a porous particle
b   stoichiometric coefficient of solid reactant B
C   concentration at time t
C_A concentration of gas A at time t
C_{AO} initial concentration of reactant A outside the particle
CV   coefficient of variation
d   stoichiometric coefficient of solid product D
D_e effective inter-diffusion coefficient
D_g diffusivity of gas in the reaction products formed on a grain
F_g shape factor of non-porous particle or grain
F_p shape factor of porous particle
g_{F_g} dimensionless time for purely chemical reaction-control
h_D mass transfer coefficient
k   reaction rate-constant
l_0 initial thickness of flat disc
L.L.   lower limit
M_B molecular mass of solid reactant B
M_D molecular mass of solid product D
n   order of reaction; variable number
$p_{F_g}(X)$ dimensionless time for a nonporous grain in internal diffusion control
$p_{F_p}(X)$ dimensionless time for a porous particle in internal diffusion control
$q_{F_g}(X)$ dimensionless time for a porous particle in external diffusion control
Q   Activation Energy
r   correlation coefficient
r_0 initial radial distance in the spherical or cylindrical porous or non-porous particle
R   universal gas constant
Sh*   modified Sherwood number

for a grain $= \dfrac{h_D F_g V_g}{D_g A_g}$

for a porous particle $= \dfrac{h_D F_p V_p}{D_e A_p}$

t   time
t^* dimensionless conversion time (t/t_{ch})

t_{ch} time for total conversion with chemical reaction
T   temperature
U.L.   upper limit
V_g volume of a grain
V_p volume of a porous particle
X_A fractional conversion of the reactant A
Z   ratio of volumes of solid reactant to solid product
δ_n small change in the reaction order
ϕ_g^2 Thiele modulus for a grain
ϕ_p^2 Thiele modulus for a particle
ρ_B density of the solid reactant
ρ_D density of the solid product
σ standard deviation
τ total conversion time

9. REFERENCES

1.   Talley, P. K., "Thermochemical Data Bases for Metallurgy", Abstract Bulletin, Fourth Biennial Conference and Workshop on Computer Software for Chemical and Extractive Metallurgy Calculations, Univ. of Missouri-Rolla, (June 7-11, 1992), 10.
2.   Bale, C. W. and Eriksson, G., "Metallurgical Thermochemical Databases-a Review", *Can. Metall. Q.*, Vol. 29, (1990), 105-132.
3.   Morris, A. E., Stephenson, J. B. and Wadsley, M. W., "Software for Chemical and Extractive Metallurgy", *J. of Metals*, Vol. 42, (1990), 35-38.
4.   Eriksson, G. and Pelton, A. D., "Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the $MnO-TiO_2$, $MgO-TiO_2$, $FeO-TiO_2$, $Ti_2O_3-TiO_2$, Na_2O-TiO_2 and K_2O-TiO_2 Systems", *Metallurgical Transactions B*, Vol. 24B, No. 5, (1993), 795-805.
5.   Heuzey, M. C. and Pelton, A. D., "Critical Evaluation and Optimization of the Thermodynamic Properties of Liquid Tin Solutions", *Metallurgical and Materials Transactions B*, Vol. 27B, No. 5, (1996), 811-828.
6.   Park, Y. G. and Gaskell, D. R., "The Thermodynamic Activities of Copper and Iron in the System Copper-Iron-Platinum at 1300 ºC", *Metallurgical Transactions B*, Vol. 20B, No. 2, (1989), 127-135.
7.   Zhao, J. C. and Henry, M. F., "The Thermodynamic Prediction of Phase Stability in Multicomponent Superalloys", *JOM*, Vol. 54, No. 7, (2002), 42-45.
8.   Asta, M., Ozolins, V. and Woodward, C., "A First-Principles Approach to Modeling Alloy Phase Equilibria", *JOM*, Vol. 53, No. 9, (2001), 16-19.
9.   Anavi, S. and Watanasiri, S., "Metallurgical Simulation with Aspan Plus", *Abstract Bulletin, Fourth Biennial Conference and Workshop on Computer Software for*

Chemical and Extractive Metallurgy Calculations, Univ. of Missouri-Rolla, (June 7-11, 1992), 24.

10. Morris, A. E. and Stephenson, J. B., "Computer Software for Chemical and Extractive Metallurgy Calculations", *J. of Metals*, Vol. 45, No. 4, (1993), 29-31.

11. Peter, S., Charette, A., But, R. T., Sett, A. T. and Potocnik, V., "An Extended Two-Dimensional Mathematical Model of Vertical Ring Furnaces", *Metallurgical and Materials Transactions B*, Vol. 27B, No. 2, (1996), 297-304.

12. Bale, C. W. and Pelton, A. D., "Optimization of Binary Thermodynamic and Phase Diagram Data", *Metallurgical Transactions B*, Vol. 14B, No. 1, (1983), 77-83.

13. Rao, Y. K., "The Analysis and Calculation of Equilibria in Complex Metallurgical Systems", *Metallurgical Transactions B*, Vol. 14B, No. 4, (1983), 701-710.

14. Kundrat, D. M., "Conceptual Model of the Iron Blast Furnace Considering Thermodynamic and Kinetic Constraints on the Process", *Metallurgical Transactions B*, Vol. 20B, No. 2, (1989), 205-226.

15. Li, Y. and Ratchev, I. P., "Rate of Interfacial Reaction between Molten $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_xO$ and $CO\text{-}CO_2$", *Metallurgical and Materials Transactions B*, Vol. 33B, No. 5, (2002), 647-790.

16. Zhao, J. C., Jackson, M. R., Peluso, L. A. and Brewer, L. N., "A Diffusion-Multiple Approach for Mapping Phase Diagrams, Hardness, and Elastic Modulus", *JOM*, Vol. 54, No. 7, (2002), 42-45.

17. Rajamani, K. and Sohn, H. Y., "Kinetics and Sulfur Fixation in the Reduction or Oxidation of Metal Sulfides Mixed with Lime", *Metallurgical Transactions B*, Vol. 14B, No. 2, (1983), 143-312.

18. Palencia, I., Romero, R., Iglesias, N. and Carranza, F., "Recycling EAF Dust Leaching Residue to the Furnace: A Simulation Study", *JOM*, Vol. 51, No. 8, (1999), 28-32.

19. Laidler, K. J., "Chemical Kinetics", McGraw-Hill, (1965).

20. Levsnspiel, O., "Chemical Reaction Engineering", 2nd Ed., John Wiley, (1972).

21. Szekely, J., Evans, J. and Sohn, H. Y., "Gas-Solid Reactions", Academic Press, N. Y., (1976).

22. Sohn, H. L., "Gas-Solid Reactions in Extractive Metallurgy", *Metallurgical Treatises*, *TMS-AIME*, (1981), 23-39.

23. Rarnachandran, P. A. and Dudukovic, M. P., "Reactions of Solid Particles with Nonuniform Distribution of Solid Reactant", *Chemical Engineering Science*, Vol. 39, No. 4, (1984), 669-680.

24. Mazet, N., "Modeling of Gas-Solid Reactions. 1. Nonporous Solids"; *International Chemical Engineering*, Vol. 32, No. 2, (1992), 271-284.

25. Mazet, N. and Spinner, B., "Modeling of Gas-Solid Reactions. 2. Porous Solids", *International Chemical Engineering*, Vol. 32, No. 3, (1992), 395-408.

26. Srolovitz, D. J., Dandy, D. S., Butler, J. E., Battaile, C. C. and Paritosh, "The Integrated Multiscale Modeling of Diamond Chemical Vapor Deposition", *JOM*, Vol. 49, No. 9, (1997), 42-47.

27. Sadrnezhaad, K., Gharavi, A. and Morvarid, O., "Simulation of Kinetics of Chemical Reactions", *Abstract Bulletin*, *Fourth Biennial Conference and Workshop on Computer Software for Chemical and Extractive Metallurgy Calculations*, Univ. of Missouri-Rolla, (June 7-11, 1992), 26.

28. Robertson, D. G. C. and Nelson, L. R., "SMAK: Kinetics of Slag-Metal-Gas Reaction in Smelting and Refining", *Abstract Bulletin*, *Fourth Biennial Conference and Workshop on Computer Software for Chemical and Extractive Metallurgy Calculations*, Univ. of Missouri-Rolla, (June 7-1l, 1992), 25

29. Orehotsky, J. and Kaczenski, M., "The Kinetics of the Hydrogen Reduction of MoO_2 Powder", *Materials Science and Engineering*, Vol. 40, (1979), 245-250.

30. H. Sharif, "The Kinetics of the Direct Reduction of Molybdenite", M.Sc. Thesis, Sharif University of Technology, (1994).

31. Mankhand, T. R. and Parsad, P. M., "Lime-Enhanced Hydrogen Reduction of Molybdenite", *Metallurgical Transactions B*, Vol. 13B, (1982), 275-282.

32. Sinadinovic, D. S. and Durkovic, B. B., *Glag. Hem. Drus. Beograd.*, Vol. 40, (1975) 539: Cited by Parsad, P. M. and Mankhand, T. R., "Hydrogen Reduction of Metal Sulfides", *Trans. of The Indian Institute Metals*, Vol. 32, No. 3, (1979), 253-285.