Kinetics of the Methane-steam Reaction

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A kinetic study was made of the reaction of steam and natural gas over a reduced nickel catalyst at a temperature range of 637° to 1,180°F.

The rate of reaction is first order with respect to methane. The effect of temperature could be expressed by an Arrhenius type of equation. Both carbon monoxide and carbon dioxide are formed as primary reaction products.

The reaction of methane and steam has assumed a position of major importance as a source of hydrogen and as a synthesis gas for oxygenated derivatives such as alcohols, aldehydes, and ketones as well as high-molecular-weight hydrocarbons. The reforming of methane with steam followed by the Fischer-Tropsch synthesis provides a possible path for conversion of methane to higher hydrocarbons.

Numerous investigators have studied the catalytic reactions for the oxidation of methane with steam and with metal oxides(*2, 7, 9, 11, 12*) and the thermal decomposition of methane(*4, 5, 6, 10, 13, 14*), and various catalysts have been developed(*3, 7*). The reverse reaction has been studied extensively at the lower temperatures by several investigators(*1, 8, 15*). However, a kinetic study of the catalytic reaction of steam and methane has not been reported. The present study is concerned with the determination of the effect of the composition on the rate of reaction of steam and natural gas on a reduced nickel catalyst at a temperature of approximately 1,180°F. and 1 atm. pressure.

APPARATUS

A diagram of the apparatus is shown in Figure 1. In order to facilitate the description of the apparatus, it will be considered as in operation. Distilled water was fed from a constant-head source through a needle valve and a capillary orifice into the preheater, which consisted of a 1-in. pipe containing porous-clay chips; the pipe was inserted in a small electric furnace. The natural gas passed through a dry test meter to a small compressor equipped with a needle-valve by-pass arrangement. The compressor was operated only at high flow rates. The steam from the preheater then mixed with the natural gas and was admitted directly into the reactor.

The reactor consisted of a piece of 2-in. pipe with a welded connection at the upstream end and a blank flange at the downstream end inserted in a 2-kw. electric furnace. Passing through the blank flange was a 1/8-in. pipe to which was welded a small cup fitted with a screen upon which the catalyst was placed. A 1/4-in. steel tube was also inserted in the blank flange to serve as a thermowell. A chromel-alumel thermocouple was placed in the thermowell immediately above the catalyst bed and a second thermocouple was placed in the center of the screen on the same level as the single layer of catalyst.

Upon entering the reactor the gases passed from the 2-in. pipe downward through the catalyst bed and out the 1/8-in. pipe to a water-cooled condenser. The condensate was removed continuously by a U-tube drain and weighed. The saturated product gases passed on through a sampling cock and then to a wet test meter.

The arrangement of the catalyst in the reactor was unique in that radiant heat supplied the energy necessary for the highly endothermic reaction. The catalyst bed was approximately 1.5 in. wide and 3.5 in. long. The bed was centered in the 2-in. pipe which formed the reactor wall. Thus the catalyst was exposed to radiant heat on all sides. It is believed that temperature variation in the bed was at a minimum.

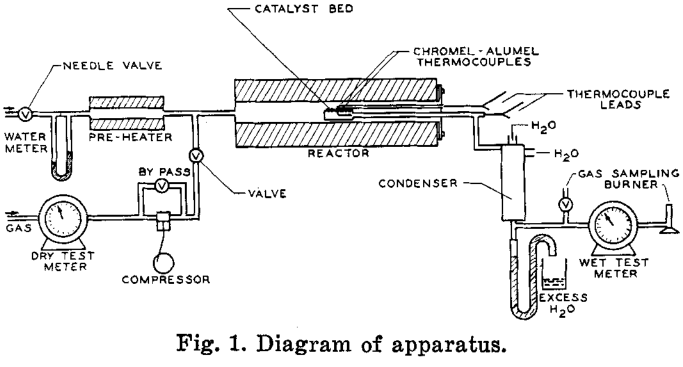

Fig. 1. Diagram of apparatus.

EXPERIMENTAL PROCEDURE

After the condenser and the thermocouple leads were disconnected, the flange was uncoupled and the catalyst assembly was removed from the reactor tube. A weighed amount of catalyst was placed on the screen. The area of the screen opening was varied by the use of sheet metal so that the catalyst completely covered the open area with a single layer. The catalyst assembly and connections were then placed back in the reactor.

The reactor then was brought up to temperature and the feeding of water begun. The water feed rate was adjusted prior to the introduction of the gas. For a series of runs the water feed rate was held constant while the natural-gas feed rate was varied to the desired feed compositions. Constant conditions were maintained for 1/2 hr. before sampling was begun. The rate of flow of gas through both meters, the water flow rate, the rate of water condensing from the product gases, and the temperatures of the gases in the catalyst bed were recorded. The product gases were analyzed according to standard procedures(*16, 18*). The carbon dioxide was determined by absorption in potassium hydroxide solution; the carbon monoxide and hydrogen by oxidation over copper oxide at 300°C.; the oxygen by absorption in Pyrogallol solution. The amounts of oxygen obtained were sufficiently small to be neglected. The ethane and heavier hydrocarbons in the product gases were not present in sufficient quantity to be detected by high-temperature oxidation techniques. Hence the gas remaining after carbon monoxide and hydrogen removal was taken as methane in all runs.

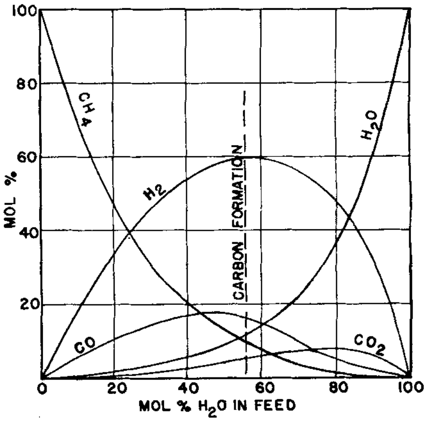

Fig. 2. Product equilibrium composition of methane-steam reaction at 1180°F.

MATERIALS

The catalyst used in this investigation was furnished by the Harshaw Chemical Company. It was a reduced nickel catalyst supported on Kieselguhr. The catalyst pellets were ⅛-*in. cylinders*. The bulk density was 93 lb./cu.ft. The composition of the natural gas is given in Table 1.

TABLE 1.—COMPOSITION OF NATURAL GAS

Component	Mole%
CO_2	00.80
CH_4	91.09
C_2H_6	5.02
C_3	1.85
iC_4	0.29
nC_4	0.24
nC_5	0.10
N_2	0.51
	99.90

TABLE 2.—PARTIAL PRESSURES AT VARIOUS TIME FACTORS

Temperature, 1,180° F.

Run	Time factor	Partial pressure of products (atm.) CH_4	H_2O	CO_2	H_2	CO
100	0.00	0.089	0.911	0.000	0.000	0.000
101	1.49	0.079	0.865	0.010	0.046	0.001
102	2.94	0.069	0.839	0.013	0.079	0.002
103	4.47	0.060	0.812	0.023	0.103	0.003
104	5.96	0.052	0.793	0.028	0.127	0.004
105	11.42	0.032	0.698	0.041	0.220	0.009
106	8.90	0.041	0.712	0.036	0.204	0.007
200	0.00	0.167	0.833	0.000	0.000	0.000
201	0.74	0.149	0.749	0.016	0.083	0.003
202	1.47	0.120	0.722	0.022	0.132	0.005
203	2.23	0.111	0.668	0.035	0.178	0.008
204	2.98	0.096	0.621	0.046	0.227	0.011
205	5.71	0.055	0.498	0.070	0.353	0.024
206	6.12	0.062	0.487	0.067	0.361	0.024
300	0.00	0.222	0.777	0.000	0.000	0.000
301	0.49	0.199	0.668	0.020	0.108	0.005
302	0.99	0.162	0.623	0.029	0.175	0.011
303	1.49	0.151	0.575	0.043	0.223	0.012
304	1.99	0.134	0.523	0.050	0.274	0.019
305	3.81	0.161	0.355	0.076	0.458	0.050
306	5.86	0.044	0.353	0.078	0.480	0.045
307	6.12	0.071	0.343	0.076	0.466	0.044
400	0.00	0.280	0.720	0.000	0.000	0.000
401	0.37	0.245	0.605	0.022	0.128	0.008
402	0.74	0.198	0.544	0.033	0.208	0.017
403	1.12	0.193	0.512	0.040	0.236	0.019
404	1.49	0.173	0.468	0.047	0.289	0.024
405	5.86	0.062	0.247	0.077	0.545	0.071
406	6.12	0.070	0.230	0.078	0.560	0.063
		Time factor = 2.98 for entire 500 series				
	Temperature, °F.					
500		0.256	0.744			
501	637	0.239	0.719	0.009	0.033	0.000
502	749	0.218	0.635	0.026	0.114	0.007
503	842	0.197	0.552	0.042	0.205	0.005
504	943	0.158	0.504	0.054	0.272	0.012

EXPERIMENTAL RESULTS

The thermodynamic relationships of the methane-steam reactions fix within rather narrow limits the temperature for a kinetic study. At temperatures below 1,100°F. the equilibrium conversion of methane is so low that the reaction has little practical interest. As the temperature is increased, the conversion increases, but the possibility of forming carbon is also greatly enhanced. At temperatures above 1,800°F. the feed gas must contain a large excess of steam in order to prevent carbon formation and thereby limit greatly the range of composition that may be studied. For these reasons a temperature of approximately 1,180°F. was chosen. At this temperature feed compositions containing up to 42 mole % methane can be used without encountering conditions that are thermodynamically favorable to carbon formation; moreover, the equilibrium conversion of methane is high.

The experimental data for this investigation may be grouped into five series, each run within a series having the same feed composition. The first four series were obtained at a temperature of approximately 1,180°F. The fifth was run over the temperature range of 637° to 1,180°F. in order to determine the effect of temperature on the reaction. The data for the five series are presented in Table 2. The reaction time for the methane is directly proportional to the amount of catalyst and inversely with the methane feed rate. This reaction time is expressed as a time factor, defined as the weight of the catalyst divided by the feed rate of the natural gas expressed as moles per hour.

In order to determine the effect of time on the activity of the catalyst, one run was made over a period of 6.5 hr. the temperature and feed rates being held constant. Samples of the product gas were analyzed periodically. During this period no change in the product-gas composition was noted. Since the catalyst was not in use more than 5 hr., the activity of the catalyst is assumed to be constant for all runs at the same temperature.

A component material balance was made for each of the runs. The average deviation for the carbon, hydrogen, and oxygen was 4.9%. The maximum deviation was 15.1%. In general, fewer atoms of carbon were measured in product gas than in the reactants, indicating that carbon was deposited in the reactor. However the hydrogen and oxygen balance did not necessarily substantiate this. No traces of carbon were observed in the reactor after a series of runs. Since the deviations were random in nature, showing no trend with composition or contact time, it is believed that they represent experimental error.

THERMODYNAMIC ANALYSIS

The over-all reaction of methane and steam to form carbon, carbon monoxide, carbon dioxide, and hydrogen may be represented by the following six equations:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \tag{1}$$

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2 \tag{2}$$

$$CH_4 \rightleftarrows C + 2H_2 \tag{3}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (4)$$

$$CO_2 + CH_4 \rightleftarrows 2CO + 2H_2 \qquad (5)$$

$$2CO \rightleftarrows C + CO_2 \qquad (6)$$

The heats and free energies of reaction for these six as computed by Wagmon et al.(*17*) were used. Using these values at 1,180°F. for reactions (1), (2), (4) and (5), the authors computed the equilibrium composition of the product gases for various feed compositions. The resulting composition diagram is shown in Figure 2. Then by means of these compositions, reactions (3) and (6) were checked to determine whether carbon might be present in an equilibrium mixture. With less than 58 mole % water in the feed, carbon may be deposited. At higher water concentrations carbon would not be present in an equilibrium mixture. This does not imply that carbon will not be formed when methane and steam react at concentrations greater than 58% water, merely that the equilibrium mixture will not contain carbon. As the reactions proceed to equilibrium, it is quite probable that carbon formation will be favored thermodynamically at one or more points along the way.

In order to determine the possible directions of the six reactions, the difference in free energy between the actual product composition and the equilibrium value for each of the six reactions was computed for the runs. The calculations indicated that

1. For all runs reactions (1) and (2) are proceeding to the right, approaching equilibrium at the longer contact times.
2. Reaction (3), if proceeding, will go to the right. However, several points taken at high contact time indicate the tendency for the reaction to reverse. This suggests that the reaction is proceeding at an extremely slow rate, or not at all.
3. In most of the runs reaction (4) has a tendency to go to the right. Points with higher inlet methane concentrations and longer contact times indicate a tendency to go to the left. This suggests that reaction (4), if proceeding, is going at a much slower rate than the reactions.
4. In all cases reaction (5) has a tendency to go to the right and reaction (6), to the left.

On the basis of these thermodynamic calculations, reactions (1) and (2) are the primary reactions and reaction (5) may be a secondary reaction. If reaction (4) is proceeding, the rate is slower. If carbon is formed, it is caused by the cracking of methane. However, it is probable that any carbon formed by reaction (3) would be consumed by the reverse of reaction (6).

In order to verify that both reactions (1) and (2) are primary reactions, the moles of carbon dioxide per mole of methane reacted for each series are plotted vs. time factor in Figure 3. The extrapolation of these curves to zero time factor indicates the initial products of reaction. From the plot it is evident that both carbon dioxide and carbon monoxide are primary reaction products. If either had been formed as a result of a secondary reaction [reaction (4)], the curves would have intersected the ordinate at unity or zero. The carbon dioxide is being formed at an initial rate of two to nine times the rate of carbon monoxide formation, depending on the inlet composition.

KINETIC ANALYSIS

If the reaction rate, r, is expressed as the moles of methane reacting per unit weight of catalyst per unit time, the relationship for a steady-flow system between conversion, weight of catalyst, and feed rate can be expressed:

$$-F\,dx = r\,dW$$

where

F = methane feed rate, moles/hr.
x = conversion, moles of methane reacted/mole of methane in feed
W = weight of catalyst
r = reaction rate, moles/unit weight of catalyst/unit time

This equation may be rearranged to give

$$r = -\frac{dx}{d\left(\frac{W}{F}\right)} = -\frac{d\frac{(CH_4)}{(CH_4)_F}}{d\,(\text{T. F.})} \qquad (1)$$

where T.F. is the time factor, weight of catalyst/mole of methane fed/hr.

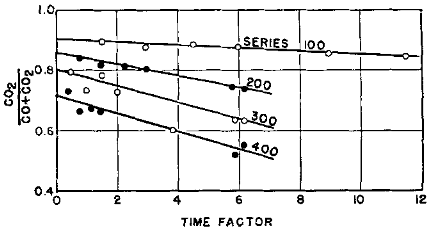

Fig. 3. Product-distribution plot.

In this study natural gas rather than pure methane was used because of the industrial interest in the reforming of natural gas to produce hydrogen. However, at even the shortest contact times none of the heavier hydrocarbons could be detected in the product gases. Thus the data constitute a kinetic study of the rate of reaction of methane. It was not possible to measure the rates of reaction of the heavier components by the techniques employed in this work; however, the presence of the components does not affect the study of the methane reaction.

If the moles of methane that have reacted per entering mole of methane are plotted vs. the time factor, the slope of the curve represents the rate of reaction at the conditions existing at that point. Although the method of slopes is, in general, subject to considerable error, the slope at the origin can be determined with a high degree of accuracy. This slope is the initial rate of reaction. The initial rate is dependent only upon the entering feed composition at a specified temperature and total pressure.

This analysis indicated that the initial rate of reaction was directly proportional to the partial pressure of methane; that is,

$$-\frac{d\frac{(CH_4)}{(CH_4)_F}}{d\,(\text{T. F.})} = kp_{CH_4} \qquad (2)$$

In order to determine whether the reaction rate was first order at appreciable concentrations of product, Equation (2) was integrated to give

$$-\int \frac{d\frac{(CH_4)}{(CH_4)_F}}{p_{CH_4}} = k\,(\text{T. F.}) \qquad (3)$$

and the integral data used for correlation. The over-all reaction can be completely described by reactions (1) and (2) if no carbon is formed. In each of these reactions the change in the total number of moles per mole of methane reacted is two. The value of the integral of Equation (3), therefore, is independent of the relative amounts of carbon monoxide and carbon dioxide. Hence, a general plot of the integral vs. the fraction of methane converted for each of the four inlet compositions could be prepared without specific knowledge of the product composition. When the fraction of methane converted from the product analysis was obtained, the corresponding value of the integral was read from the curve and plotted vs. the time factor. If the reaction is first-order over the whole range of compositions, the resulting curve would be a straight line with a slope equivalent to k, the reaction velocity constant. This plot is given in Figure 4. The data define a straight line quite well. The points not falling on the curve are at very low concentrations of methane, where small analytical errors are greatly magnified.

The rate of reaction being directly proportional to the methane partial pressure suggests two possible mechanisms as the rate-controlling step: (1) the mass transfer of the methane to the catalyst surface and (2) a first-order reaction, either the chemisorption of the methane on the active centers of the catalyst or the decomposition of the adsorbed methane to form free radicals. Of the two mechanisms, only the rate of mass transfer is dependent on the gas velocity through the catalyst bed. Since the diffusivities of methane, carbon dioxide, carbon monoxide, and water are of the same order of magnitude, it is not probable that the rate of diffusion of only one, methane, would be rate controlling. In order to check the effects of mass transfer, several runs were made in which the gas velocity through the bed was doubled but at the same time factor as the previous runs. For these runs the reaction velocity constant increased 10 to 15%, as compared to a theoretical increase of over 50% if mass transfer alone were rate controlling, thus indicating that mass transfer may have an appreciable effect. However, the reaction is highly endothermic, and an increase in gas velocity might quite easily result in an increased temperature at the catalyst surface, thus increasing the rate of reaction. It was not possible to make a systematic study of the effect of gas velocity in this experimental set-up. Consequently the only conclusion that can be drawn is that the gas velocity through the bed does have a slight effect on the rate of reaction and this effect is possibly due to mass transfer.

A first-order rate process would describe both the chemisorption of methane and the decomposition of the chemisorbed methane. In the former the rate of adsorption is directly proportional to the partial pressure if the surface is sparsely covered with methane. For the latter case the partial pressure of methane would be proportional to the concentration of the chemisorbed methane, since the adsorption step could be assumed to be at equilibrium. This first-order process is in agreement with the kinetics of the decomposition reaction of methane. Kassel(*10*) found that the thermal decomposition was first order and that the rate-controlling step was probably the reaction

$$CH_4 \rightleftarrows CH_2 + H_2$$

Moreover, the decomposition of higher hydrocarbons is generally first order for both thermal and catalytic reactions.

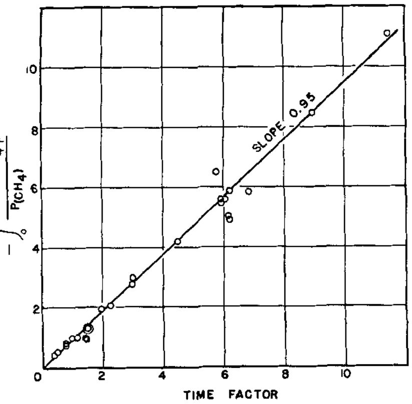

Fig. 4. First-order integral rate vs. time factor.

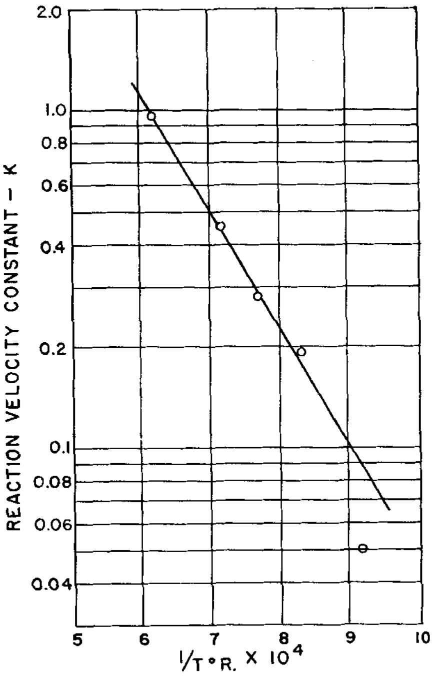

Fig. 5. Reaction-velocity constant vs. reciprocal of absolute temperature.

The reaction velocity constants can be expressed as a function of temperature by the Arrhenius equation

$$\frac{d \ln k}{dT} = \frac{Ea}{RT^2} \tag{4}$$

or in the integrated form

$$k = Ae^{-\frac{Ea}{RT}}$$

where Ea is the apparent energy of activation for the reaction.

A series of runs was made at a constant-feed composition and a constant-time factor over the temperature range of 637° to 1,180°F. in order to measure the effect of temperature on the reaction velocity constant. The energy of activation, as defined by Equation (4), can be evaluated by measuring the slope of the curve $\ln k$ vs. the reciprocal of the absolute temperature. Such a plot is given in Figure 5. The reaction velocity constant can be represented by the equation

$$k = 127e^{-\frac{15{,}800}{RT}}$$

A kinetic analysis of the data reported by Bischel(*2*) using the same catalyst in a conventional fixed-bed reactor over the temperature range of 900° to 1,100°F. is in excellent agreement with these results.

The energy of activation of 15,800 B.t.u./lb. mole is of the same order of magnitude as that of radical formation for methane decomposition. If mass transfer were rate controlling, the rate constant would have increased less than twofold over the temperature range studied instead of tenfold, as found experimentally.

CONCLUSIONS

The rate of reaction of methane and steam over a reduced nickel is first order with respect to methane. The results indicate that the rate-controlling step is the decomposition of methane. Mass transfer, although not rate controlling, may exert an effect on the rate, but the data were not sufficient to evaluate this effect. Both carbon dioxide and carbon monoxide are primary reaction products, the carbon dioxide being formed from two to nine times faster than carbon monoxide. The water-gas shift reaction, if proceeding at all, is at a much slower rate.

NOTATION

A = constant of integration
Ea = apparent energy of activation, B.t.u./(lb. mole) (°R.)
F = feed rate, moles methane/hr.
T = temperature, °R.
T.F. = time factor, lb. catalyst/mole methane fed/hr.
W = weight of catalyst, lb.
(CH_4) = mole methane
k = reaction velocity constant, moles/(hr.) (lb. of catalyst) (atm.)
pCH_4 = partial pressure of methane, atm.
r = reaction rate, moles/(hr.) (lb. of catalyst)
x = conversion, moles/mole

Subscript

F = feed

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Graphical Solutions on Dimensionless-number Plots

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A graphical method for solving problems involving dimensionless-number plots is presented, and its application demonstrated for the relatively involved case of liquid cyclone scale-up.

Dimensionless-number plots frequently are awkward to use, in that the dependent variable, or unknown, may be contained in more than one of the dimensionless-number groups. In such a case there has been no direct way to solve for the unknown. Before the unknown could be evaluated, roundabout calculations have had to be made in order to locate the appropriate point on the dimensionless-number plot.

By way of example the familiar log-log plot of drag coefficient vs. Reynolds number, shown as Figure 1, may be considered. This relates to the free settling of spherical particles in a fluid. In actual problems which arise the unknown is most frequently either terminal settling velocity u_p or particle size D_p, both of which are included in each of the two dimensionless groups. When either u_p or D_p is unknown, the value for Re cannot be calculated directly, and neither can the value for C_R. Neither coordinate on the dimensionless-number graph, therefore, can be evaluated directly, and further means must be employed to find where on the graph the problem operation should be plotted.

One method for solving sedimentation problems when either u_p or D_p is unknown involves replotting the information of Figure 1 on a graph of Re vs. a new dimensionless function $C_R Re^n$, the exponent n being so chosen that the unknown variable, either u_p or D_p, cancels out of the function. Since the new function does not contain the unknown, it can be evaluated directly. The corresponding value of Re can thus be determined by means of the new graph, and the unknown calculated from the discovered value of Re.

There is also a graphical construction(*1*) for discovering the appropriate value of Re, in which the function

$$\log C_R = -n \log Re + \log C_R Re^n \quad (1)$$

is plotted in Figure 1. Here again the exponent n is chosen so that the unknown cancels from the final term, which can therefore be evaluated. The intersection of the plot of Equation (1) with that originally constituting Figure 1 locates the required Re value, namely, Re', from which the unknown can be calculated.

Neither of the methods described provides a graphical element to measure the value of the unknown. In this paper the graphical method will be elaborated to permit representing the unknown directly, and the particular utility of the method will be demonstrated in connection with solid-liquid cyclone scale-up problems.

GRAPHING AS A VECTOR ADDITION

Graphing, at least in Cartesian coordinates, may be regarded as a