Chen, J. C., "Heat Transfer to Tubes in Fluidized Beds," ASME Paper 76-HT-75, ASME-AIChE Heat Transfer Conf., St. Louis, MO (1976).

Glass, D. H., and D. Harrison, "Flow Patterns Near a Solid Obstacle in a Fluidized Bed," *Chem. Eng. Sci.*, **19**, 1001 (1964).

Hager, W. R., and W. J. Thomson, "Bubble Behavior around Immersed Tubes in a Fluidized Bed," *AIChE Symp. Ser.*, **69**, (128), 68 (1973).

Kunii, D., and O. Levenspiel, *Fluidization Engineering*, John Wiley and Sons, New York (1969).

Mickley, H. S., and D. F. Fairbanks, "Mechanism of Heat Transfer to Fluidized Beds," *AIChE J.*, **1**, 374 (1955).

Nixon, T. L., "Circuit Design for Capacitance Probes," Instrumentation Lab., ME and Mech Dept., Lehigh University, Bethlehem, PA (1978).

Ozkaynak, T. F., and J. C. Chen, "Average Residence Times of Emulsion and Void Phases at the Surface of Heat Transfer Tubes in Fluidized Beds," *AIChE Symp. Ser.*, **74**, (174), 334 (1978).

Ozkaynak, T. F., and J. C. Chen, "Emulsion Phase Residence Time and Its Use in Heat Transfer Models in Fluidized Beds," *AIChE J.*, **26**, (4), 544 (1980).

Rooney, N. M., and D. Harrison, "Flow Patterns Near Horizontal Tubes in a Gas-Fluidized Bed," *Fluidization Technology*, **II**, ed., D. L. Keairns, Hemisphere Publishing Corp., Washington, 3 (1976).

Saxena, S. C., N. S. Grewal, J. D. Gabor, S. S. Zabrodsky, and D. M. Galershtein, "Heat Transfer Between a Gas Fluidized Bed and Immersed Tubes," *Adv. Heat Trans.*, **14**, 149 (1978).

Syromyatnikov, N. I., V. M. Kulikov, V. S. Nosov, and V. N. Korolev, "The Instantaneous Local Rate of External Heat Transfer in an Inhomogeneous Fluidized Bed," *Heat Transfer—Sov. Res.*, **8**, (5), 42 (1976).

Zabrodsky, S. S., N. V. Antonishin, and A. L. Parnas, "On Fluidized Bed-to-Surface Heat Transfer," *Can. J. Chem. Eng.*, **54**, 52 (1976).

Manuscript received February 2, 1981; revision received October 26, and accepted November 5, 1981.

Experimental Measurement of the Thermal Stability Criteria for the Low Pressure Methanol Synthesis

The mathematical basis was derived for the experimental measurement of the "Slope Condition" and of the "Dynamic Condition" of the thermal stability criteria in a laboratory-scale internal recycle reactor. This work also resulted in clearer interpretations and simpler expressions for the two stability criteria. The method was experimentally demonstrated on the example of the low pressure methanol synthesis. Only seven experiments were needed to evaluate the stability criteria of this reaction for which the kinetics is unknown.

J. M. BERTY, J. P. LENCZYK and S. M. SHAH

Department of Chemical Engineering
The University of Akron
Akron, OH 44325

SCOPE

The objective of this study was to develop an experimental method for the measurement of the thermal stability criteria. These are needed for the design of thermally stable commercial reactors, including auto-thermally operated converters. The knowledge of these criteria is needed already in the early conceptual design stage of a new process, sometimes even before a detailed kinetic model can be developed.

The second objective of this work was to show that even in the absence of knowledge on the kinetics of the reaction, the basic parameters for the stability criteria can be evaluated from a few experiments. These can be made in an internal recycle reactor operating as a CSTR at, or close to, the operating conditions of anticipated commercial process. The results can be used in the design of cooled tubular, or adiabatic production reactors and the results are not dependent on any assumptions made on the kinetics. In the opposite case, when kinetics is known, these experiments can serve as checks that are independent of the assumptions made in the kinetic study.

Historically, the original work of Liljenroth (1918), Damköhler (1937), and Wagner (1945) went unnoticed while the papers of Wilson (1946) and Frank-Kamenetskii (1939, 1961) had the first impact on the industry, and Van Heerden's (1953, 1958) papers started an avalanche of theoretical investigations. In the papers of both Wilson and Frank-Kamenetskii, the thermal stability criterion is expressed as a maximum permissible temperature difference for heat removal, that is a unique function of the energy of activation. An internal report from Union Carbide by Perkins in 1938 revealed the existence of a limiting maximum temperature difference for thermally stable operation that can be calculated from the energy of activation. These are simplified functions, and express conservative estimates built on the assumption of a zero order reaction rate. Frank-Kamenetskii recognized this and modified it on the basis of geometric arguments. Although these estimates were too simple and too conservative, they served the industry better than most of the work that followed. Theoretically better criteria developed later are elegant mathematical solutions of variations of the same problem. Generalization and basic understanding has not advanced much and Luss (1980) expressed the need for these.

Schmitz (1975) in his extensive review on the subject of stability estimated that only about 40% of the published papers in the last two decades were referenced on his list that counts close to 300 papers. He estimates also that references from areas other than chemical reactions amounted to an even smaller fraction. In spite of this, it is most likely that he caught all of the approximately 45 experimental papers. Of these, only eight were made on chemical systems that could have some industrial importance. The rest of the experiments were made on model reactions, like the oxidation of H_2, to test some theoretical

---

Correspondence concerning this paper should be directed to J. M. Berty.

J. P. Lenczyk is at the R & D Center of the B. F. Goodrich Co., Brecksville, OH 44141.

S. M. Shah is at Div. of Water, Dept. of Nat. Res. and Env. Prot. of the State of Kentucky, Frankfort, KY 40601.

0001-1541-82-4468-0914-$2.00.

points.

Conceptually significant experiments on thermal stability were started by Wicke and Vortmeyer (1959) and continued by their coworkers. One experimental study on an industrially important reaction was published by Bush (1964).

Two more recent interesting publications in this field came from Uppal et al. (1974, 1976) who organized various available information on steady-state multiplicity, stability, and oscillations. Another important one is from Schmitz et al. (1979) where experimental results on a model reaction were reconciled very successfully with theory.

On the kinetics of methanol synthesis, Natta (1955) published a Langmuir-Hinshelwood type model for the Zn/Cr type catalyst that was extended by Cappelli (1965). A thorough literature search indicates there is a complete lack of data for the kinetics on the low pressure Cu-type catalysts. Also, Natta's model contains too many constants to have statistical significance and, Shinnar (1978) and Weller (1976) have shown that such a model cannot be justified either theoretically or practically.

Stephens (1975) published a paper on stability and optimization of an industrial low pressure methanol converter. He discussed the effect of an outside heat exchanger and control schemes on the auto-thermal operation without disclosing anything on the kinetics.

CONCLUSIONS AND SIGNIFICANCE

The van Heerden diagram expressing the heat generation rate as the function of temperature can be measured for industrially important catalytic reactions at, or close to, the commercial operating conditions in an internal recycle reactor. This was experimentally demonstrated on the low-pressure methanol synthesis example, for which reaction the kinetics is unknown.

The above measurement has to be made at constant feed rate, and feed concentration, with fixed catalyst quantity, i.e., at constant residence time (θ = const.). The need for this was derived for first order reactions, but holds conceptually for all others, too.

The experimentally measured van Heerden diagram is a valid representation of the process even if the assumptions made in the derivation for the first order rate example are not valid. No previous knowledge of kinetics is needed for the measurements.

The dimensionless residence time, the first Damköhler number can be evaluated from the material balance for a CSTR simply. In the case of non-stoichiometric feed mixtures and complex reactions the heat generation rate $\bar{q}_{gen}$ divided by the adiabatic temperature rise potential β and by the steady-state temperature may serve well.

The dimensionless energy of activation, the Arrhenius number $\epsilon = E/RT$ can be evaluated from experiments in a CSTR, (Berty, 1979). The dimensionless adiabatic temperature rise potential β can be calculated from thermochemical data; therefore, the expression

$$\epsilon\beta > \left[\frac{1 + Da}{Da}\right]^2 = \frac{1}{X^2}$$

can be used to demarcate the highest conversion where oscillations are still not possible and the slope criterion alone is a satisfactory condition for stability. This is the usual case in commercial processes where secondary degradation reactions limit the conversion and Da is small.

It was known that the "Slope Condition" can be expressed as an inequality of temperature derivatives of the heat removal and heat generation rates as:

$$\frac{d\bar{q}_{rem}}{dT} > \frac{d\bar{q}_{gen}}{dT}$$

Now we have shown that the second criterion named by Gilles and Hofmann (1961) as "Dynamic Condition" can be expressed in similar way as

$$\frac{d\bar{q}_{rem}}{dT} > \left.\frac{\partial \bar{q}_{gen}}{\partial T}\right|_C + \left.\frac{\partial m}{\partial C}\right|_T$$

This means that the increase of heat removal rate with the increase in temperature has to be larger than the difference between heat generation rate increase due to the temperature alone and the reaction rate decrease due to the concentration drop alone.

The significance of the criteria expressed in previous points is in their use for estimating the stability or thermal sensitivity limits for cooled tubular reactors (Bischoff and Froment, 1976), and for multi-stage adiabatic reactors with intercoolers (Berty, 1968).

THEORY

Bases for Balance Equations

The aim of this work is to find the experimental conditions that can be used to measure the important parameters and functions for the thermal stability criteria of reactions. In order to do this, first the physical meaning of the stability criteria were clarified and then the criteria were translated into experimental requirements. In the following clarification the basic work of Aris and Amundson (1958) will be interpreted beyond the explanation of Gilles and Hofmann (1961). In doing this, some changes in reference values and approaches were made to make the physical meaning of the results easier to elucidate. These are as follows:

a. The changing of the balance equations to dimensionless forms will be delayed until their derivatives need to be evaluated to keep the physical meaning easier to recognize.

b. The steady-state reaction temperature and concentration will be used for reference state in converting to dimensionless quantities because the local linearization in the temperature derivatives of the reaction rate was made around the steady state.

Especially the second change will allow great flexibility in explanations without losing any part of the rigor of the mathematical derivation by Aris and Amundson (1958). Instead of using the notation of these authors, an equivalent but simpler notation of Carra and Forni (1974) is used as is reproduced in Carberry's book (1976). The same derivation is given yet another way by retaining the variables in their original dimensions in the book of Froment and Bischoff (1979). All these approaches and what will follow have to give the same results since they are only notational variations of the same equations. The theory given next is not new, details are stressed only for clearer interpretation.

ANALYSIS OF THE BALANCE EQUATIONS FOR CSTR'S

The material balance function for CSTR is:

$$\frac{VdC}{Qdt} = C_o - C_s - (V/Q)r(C,T) \boxminus m(C,T)$$

where $r(C,T) = k(T)C^n$ refers to the power-law kinetics and n can take on any value.

In steady state $m(C,T) = 0$, and $(V/Q) = \theta$, therefore, in this case:

$$C_o - C_s = \theta k(T_s)C_s^n$$

This equation establishes unique relation between any two of the variables C_o, C_s, T_s, and θ when values are fixed for the other two. In the following, while the general nth order form will be retained to help in understanding the meaning of the expressions, from now on, the simplest case of the first order reaction will be given also. For first order reaction from the relationship given above follows:

$$C_s = \frac{C_o}{1 + \theta k_o e^{-E/RT_S}}$$

Using the definition of $Da \equiv (r_s/C_s)\theta$, where Da is the first Damköhler number, the dimensionless residence time, expressed as the residence time θ divided by the time constant for the reaction, $r_s/C_s = k$ for first order reaction.

With the Damköhler number the steady-state material balance can be expressed as:

$$\frac{C_o - C_s}{C_s} = Da$$

From this it follows that:

$$1 + Da = C_o/C_s, \text{ and the fractional conversion:}$$
$$X = (C_o - C_s)/C_o = Da/(1 + Da).$$

The partial derivative of the material balance function, $m(C,T)$ with regard to the concentration is:

$$\left.\frac{\partial m(C,T)}{\partial C}\right|_T = -1 - \theta nkC^{n-1}$$

and in dimensionless terms:

$$\partial m(C,T)/\partial C|_T = -(1 + nDa)$$

For first order reactions, when $n = 1$, this equation is:

$$\partial m(C,T)/\partial C|_T = -(1 + Da).$$

The heat balance function for a CSTR is:

$$\rho cVdT/dt = Q\rho c(T - T_o) + U_oaV(T - T_c) - (-\Delta H)Vr(C,T) = q(C,T)$$

$$q_{ad}(T) + q_{tr}(T) - q_{gen}(C,T) = q(C,T)$$

The temperature derivative of this function is:

$$Q\rho c + U_oaV - (-\Delta H)V(dr/dT) = dq(C,T)/dT$$

The partial derivative with regard to temperature is:

$$Q\rho c + U_oaV - (-\Delta H)V\partial r/\partial T|_C = \partial q(C,T)/\partial T|_C$$

The temperature derivatives of the rate of reaction are:

$$r = k_o\exp(-E/RT) \cdot C^n$$

$$\partial r/\partial T|_c = (E/RT^2)\, k_o\exp(-E/RT) \cdot C^n = (E/RT^2)r$$

$$dr/dT = (E/RT^2)\, r + n\,(r/C)(dC/dT)$$

From material balance at steady state, when C_o and θ are constant:

$$C_s = C_o/(1 + \{\theta k_o\exp(-E/RT_s)\}C_s^{n-1}).$$

For first order reaction the derivative of this becomes:

$$\frac{dC_s}{dT} = \frac{-C_o(E/RT^2)\theta k_o\exp(-E/RT)}{\{1 + \theta k_o\exp(-E/RT)\}^2},$$

therefore the temperature derivative of the rate is:

$$\frac{dr_s}{dT} = \frac{E}{RT_s^2}r\frac{C_s}{C_o},$$

this result was shown by Perlmutter (1972).

The heat balance function in temperature dimension is:

$$-\bar{q}(C,T) = T_s - T_o + \frac{U_oa\theta}{\rho c}(T_s - T_c) - \frac{(-\Delta H)r\theta}{\rho c}$$

$$-\bar{q}(C,T) = \bar{q}_{ad}(T) + \bar{q}_{tr}(T) - \bar{q}_{gen}(C,T).$$

The temperature derivative of the heat balance function is:

$$-\frac{d\bar{q}(C,T)}{dT} = 1 + \frac{U_oa\theta}{\rho c} - \frac{(-\Delta H)\theta}{\rho c}\frac{dr}{dT}$$

For first order reaction and for steady state $dr_s/dT = (E/RT_s^2)r(C_s/C_o)$, therefore:

$$-\frac{d\bar{q}(C,T)}{dT} = 1 + \frac{U_oa\theta}{\rho c} - \frac{(-\Delta H)\theta}{\rho c}\frac{E}{RT_s^2}r_s\frac{C_s}{C_o},$$

and in dimensionless terms this equation becomes:

$$-\frac{d\bar{q}(C,T)}{dT} = 1 + UDa - \epsilon\beta\frac{Da}{1 + Da}, \text{ and}$$

the terms are equivalent to:

$$-\frac{d\bar{q}(C,T)}{dT} = \frac{d\bar{q}_{rem}}{dT} - \frac{d\bar{q}_{gen}}{dT},$$

where

$$\epsilon = E/RT_s;\ \beta = (-\Delta H)C_s/\rho cT_s, \text{ and}$$

$$\frac{Da}{1 + Da} = \frac{r\theta}{C_o} = \frac{\theta kC_s}{C_o} = Da\frac{C_s}{C_o} = X.$$

The partial derivative of the heat balance function with respect to the temperature is:

$$-\left.\frac{\partial\bar{q}(C,T)}{\partial T}\right|_C = 1 + \frac{U_oa\theta}{\rho c} - \frac{(-\Delta H)\theta}{\rho c}\left.\frac{\partial r}{\partial T}\right|_C.$$

For first order reaction the partial derivative is:

$$-\left.\frac{\partial\bar{q}(C,T)}{\partial T}\right|_C = 1 + \frac{U_oa\theta}{\rho c} - \frac{(-\Delta H)\theta}{\rho c}\frac{E}{RT^2}r,$$

and in dimensionless terms this is:

$$-\left.\frac{\partial\bar{q}(C,T)}{\partial T}\right|_C = 1 + UDa - \epsilon\beta Da,$$

where

$$\frac{d\bar{q}_{rem}}{dT} = 1 + UDa, \text{ and } \frac{\partial\bar{q}_{gen}}{\partial T} = \epsilon\beta Da.$$

In summary it was shown that for first order reactions in steady state and for cases where the heat transfer coefficient is independent of the reaction temperature:

$$-\frac{d\bar{q}(C,T)}{dT} = 1 + UDa - \epsilon\beta\frac{Da}{1 + Da}, \tag{1}$$

$$-\left.\frac{\partial\bar{q}(C,T)}{\partial T}\right|_C = 1 + UDa - \epsilon\beta Da, \tag{2}$$

$$\left.\frac{\partial m(C,T)}{\partial C}\right|_T = -(1 + Da). \tag{3}$$

$$\frac{d\bar{q}_{gen}}{dT} = \epsilon\beta\frac{Da}{1 + Da}, \tag{4}$$

$$\left.\frac{\partial\bar{q}_{gen}}{\partial T}\right|_C = \epsilon\beta Da \tag{5}$$

The above expressions are needed to elucidate the meaning of the stability criteria and to derive the experimental requirements.

ELUCIDATION OF THE STABILITY CRITERIA

General Forms. Expression for the two stability criteria that are equivalent to those derived by Aris and Amundson (1958) can be found in Carberry's book (1976) who credits Carra and Forni (1974) with the derivation. In the following chapter, this later form of stability criteria, including their nomenclature, will be used. The reason for this is primarily that the steady-state values C_s, T_s are used for normalizing the variables and also because it is perhaps easier for the reader to have access to Carberry's book for the necessary background information.

In Carberry's book the two stability criteria are expressed as:

$$\left(1+\frac{1}{Da}\right)\left(\frac{1}{Da}+U-\epsilon\beta\right)+\epsilon\beta>0, \text{ for the slope criterion}$$

and

$$1+\frac{2}{Da}+U-\epsilon\beta>0, \quad \text{for the dynamic criterion.}$$

(In Carberry's book, on p. 134, this latter equation is identified as slope condition by typographical error.)

This can be rearranged to:

$$1+UDa-\frac{\epsilon\beta Da}{1+Da}>0, \qquad \text{(slope), and} \qquad (6)$$

$$1+UDa-\epsilon\beta Da+(1+Da)>0, \qquad \text{(dynamic).} \qquad (7)$$

These expressions are strictly valid only for first order reactions in steady state and where the heat transfer coefficient does not depend on the temperature.

Using the expressions for the ordinary and partial temperature derivatives of the heat generation function Eqs. 1 and 2 and the concentration partial of the mass balance function Eq. 3 the two criteria can be expressed as:

$$\frac{d\bar{q}}{dT}>0, \qquad \text{(slope) and}$$

$$\left.\frac{\partial\bar{q}}{\partial T}\right|_C-\left.\frac{\partial m}{\partial C}\right|_T>0, \qquad \text{(dynamic).}$$

The validity of the criteria in the derivative form are not limited to first order reactions nor to temperature independent heat transfer coefficient anymore, but for practical calculations, the proper expressions have to be substituted.

Another way of expressing the same criteria is:

$$\frac{d\bar{q}_{\text{rem}}}{dT}>\frac{d\bar{q}_{\text{gen}}}{dT}, \qquad (8a)$$

or

$$\frac{dq_{\text{rem}}}{dT}>\frac{\left.\frac{\partial q_{\text{gen}}}{\partial T}\right|_C}{-\left.\frac{\partial m}{\partial C}\right|_T}, \qquad \text{for slope} \qquad (8b)$$

and

$$\frac{dq_{\text{rem}}}{dT}>\left.\frac{\partial q_{\text{gen}}}{\partial T}\right|_C+\left.\frac{\partial m}{\partial C}\right|_T, \qquad \text{for dynamic condition.} \qquad (9)$$

Only two of the three derivatives have to be known to define both criteria since:

$$\frac{d\bar{q}_{\text{gen}}}{dT}=\frac{\left.\frac{\partial\bar{q}_{\text{gen}}}{\partial T}\right|_C}{-\left.\frac{\partial m}{\partial C}\right|_T} \qquad (10)$$

These expressions will serve as a guide for the experimental program.

Limits for Oscillation. Oscillation is possible according to Gilles and Hoffman, if the slope condition is satisfied, but the dynamic condition is not. These are expressed below in the form where the L.H.S. is the same for both, and it is the temperature derivative of the heat removal rate, as:

$$1+UDa>\epsilon\beta\frac{Da}{1+Da}, \qquad \text{(slope)}$$

$$1+UDa>\epsilon\beta Da-(1+Da), \qquad \text{(dynamic)}$$

Therefore, oscillations are possible if:

$$\epsilon\beta\frac{Da}{1+Da}<\epsilon\beta Da-(1+Da), \text{ or } \epsilon\beta>\left[\frac{1+Da}{Da}\right]^2=\frac{1}{X^2}$$

$$\text{and } \epsilon\beta\frac{Da}{1+Da}<(1+UDa)<\epsilon\beta Da-(1+Da).$$

When the opposite is true, the slope condition alone is a satisfactory criterion for stability.

The slope Condition in Original Dimensions. Writing in the original variables and parameters in the slope criterion:

$$1+UDa>\epsilon\beta\frac{Da}{1+Da}, \text{ we receive:}$$

$$Q\rho c+U_oaV>\frac{E}{RT_s^2}q_{\text{gen}}\frac{C_s}{C_o}.$$

In the "isothermal" CSTR where the feed is at the reaction temperature, hence all heat generated is removed through the walls by heat exchange, the equation further simplifies to:

$$U_oaV>\frac{E}{RT_s^2}q_{\text{gen}}\frac{C_s}{C_o}, \text{ and since } U_oaV=\frac{q_{rem}}{T_s-T_c},$$

and in steady state $q_{\text{rem}}=q_{\text{gen}}$, therefore:

$$\Delta T_{tr}<\frac{RT_s^2}{E}\frac{C_o}{C_s} \text{ and } \Delta T_{tr}=T_s-T_c.$$

The last equation is strictly valid only for first order reactions and where the heat transfer coefficient is independent of the temperature.

The expression for $\Delta T_{\max}$ derived by Frank-Kamenetskii (1961) and Wilson for zero order reactions:

$$\Delta T<\frac{RT^2}{E}$$

is a conservative estimate for positive order reactions and is good for low conversions. The expression

$$\Delta T<\frac{RT^2}{E}\frac{C_o}{C_s}$$

gives a somewhat better value for first order reactions and it is a conservative estimate for reactions higher than first order. The only parameter necessary to know is E. The $\Delta T_{\max}$ calculated from the R.H.S. of the inequality is a conservative estimate also, and it can be exceeded somewhat if the heat transfer coefficient is increasing with the temperature, as it does frequently in the presence of chemical reactions.

EXPERIMENTS

Reaction

The experimental methods for measuring the important parameters for thermal stability calculation were demonstrated on the example of the low-pressure methanol synthesis. The main, synthesis reaction:

$$CO+2H_2 \rightleftarrows CH_3OH, \ \Delta H_r^0=-97.4 \text{ kJ/mol}$$

was accompanied by the CO shift reaction in reverse:

$$CO_2+H_2 \rightleftarrows CO+H_2O, \ \Delta H_r^0=+40.3 \text{ kJ/mol}$$

because, the feed has to have some CO_2 to prevent the complete reduction of the copper-based catalyst (Kung, 1980).

The anticipated methane byproduct formation:

$$CO+3H_2 \rightarrow CH_4+H_2O, \qquad \Delta H_r^0=-205 \text{ kJ/mol}$$

was totally absent as far as could be established within the analytical errors. Since 5 mol% CH_4 was included in the feed gas to simulate industrial composition, this methane as an inert was used for internal standard to correct material and elementary balances on no-methane-change basis. The values corrected on no-change-of-methane basis are indicated with a capital M added to the name of the variable on Table showing the results of a typical experiment.

Experimental Strategy. The R.H.S. of the two stability criteria expressed in Eqs. 8 or 9 and 10, contains three derivatives:

$$\left.\frac{\partial m}{\partial C}\right|_T, \quad \left.\frac{\partial \bar{q}_{gen}}{\partial T}\right|_C, \text{ and } \frac{d\bar{q}_{gen}}{dT}$$

Of these three at least two have to be measured experimentally to estimate the two criteria.

In a recycle reactor that operates as a CSTR, rates are measured directly. Therefore, to develop the derivatives for the rates, one has to measure the rates at somewhat higher and somewhat lower value of the argument, and calculate the ratio of finite differences as approximation for the derivative, e.g.:

$$\frac{d\bar{q}_{gen}}{dT} \approx \frac{\bar{q}_{gen_2} - \bar{q}_{gen_1}}{T_2 - T_1}$$

$$\text{where } T_2 = T + \frac{1}{2}\Delta T \text{ and } T_1 = T - \frac{1}{2}\Delta T.$$

Another approach is to measure the rate as a function of its argument and then differentiate the function. The differentiation can be done either by fitting an empirical function to the curve, like Fourier series and differentiating it analytically, or plotting the function and differentiating it graphically.

This latter method was used here because it illustrates the method better. In these measurements, the highest possible heat and mass transfer condition should be maintained to assure unique steady states in all experiments.

The Partial Derivative of the Material Balance Function, with regard to concentration, can be measured since:

$$\left.\frac{\partial m}{\partial C}\right|_T = -\left(1 + \theta \left.\frac{\partial r}{\partial C}\right|_T\right),$$

by measuring the rate at various steady-state concentrations by changing the feed rate, i.e., residence time at constant feed concentrations and temperature. This results in the function of:

$$r = f(C), \text{ at const. } C_o \text{ and } T.$$

Plotting r vs. C and differentiating it will give $\partial r/\partial C|_T$. Multiplying this with the corresponding residence time, and adding one, will result in the desired expression. The use of this measurement for the determination of the overall order of a reaction was shown in a previous paper (Berty, 1979).

The main difficulty here is the lack of knowledge of which concentration to use for argument in systems with multiple reactions and non-stoichiometric feed concentrations.

The partial derivative of the heat generation rate with regard to the temperature can be measured considering that:

$$\left.\frac{\partial \bar{q}_{gen}}{\partial T}\right|_C = \frac{(-\Delta H)\theta}{\rho c} \left.\frac{\partial r}{\partial T}\right|_C$$

by measuring the rate at various temperatures as:

$$r = f(T), \text{ at constant } C_0 \text{ and } C.$$

This is done with constant feed concentration and by keeping the steady-state concentration constant through adjustment of the feed rate, and with it the residence time. Differentiating the curve with temperature will give $\partial r/\partial T|_C$. The minor changes in value of $(-\Delta H)/\rho C$ with temperature can be neglected and this can be considered as a constant multiplier. If warranted, calculating this value for every measurement temperature can be done before multiplying the rate with it, to get a more precise heat generation rate. The product has then to be multiplied with the θ corresponding to the C value. The use of the measurement of r at various values of T with constant C_o and C_s was shown in previously cited paper for the estimation of the energy of activation.

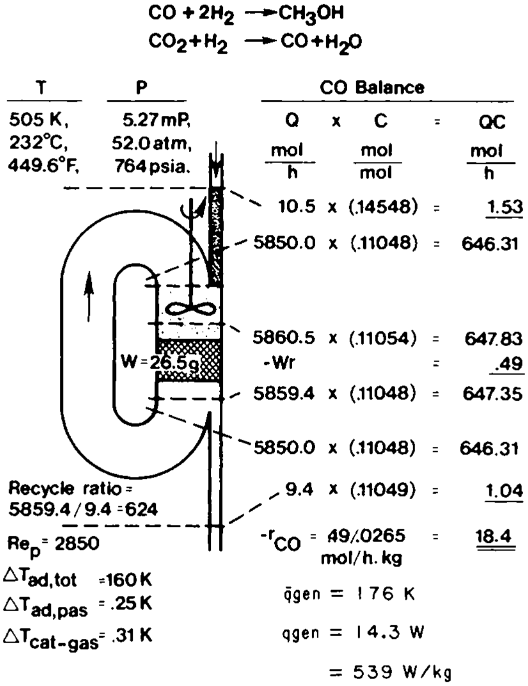

Figure 1. Experiment: methanol synthesis.

The ordinary derivative of the heat generation rate with regard to temperature:

$$\frac{d\bar{q}_{gen}}{dT} = \frac{(-\Delta H)\theta}{\rho C} \cdot \frac{dr}{dT}, \text{where } r = f_1(T,C) \text{ and } C = f_2(T)$$

at fixed θ. Therefore, measuring the rate at fixed θ and C_o at various temperatures, where C will vary to correspond to C_s at the given temperature, will give $r = f_1(T,f_2(T))$. This multiplied with the practically constant $(-\Delta H)\theta/\rho c$) will result in $\bar{q}_{gen}$. A plot of the heat generation rate vs. the temperature is usually called the Van Heerden diagram. Differentiating this curve at given values of T gives then $d\bar{q}_{gen}/dT$ at these values of the argument. These measurements are reported in this paper.

Apparatus. The internal recycle reactor developed by Berty (1969, 1974) was used for the experimental study. Recycle reactors at high recycle ratios approximate the perfect CSTR operation very well.

A conceptual diagram of the recycle reactor is shown on Figure 1, with the data of an actual experiment added, with details given on Table 1. The standard 127 mm (5 in.) I.D. recycle reactor and the full experimental system was made by Autoclave Engineers, Inc. A sketch for the reactor and the flow sheet for the experimental unit was given elsewhere (Berty, 1979).

While physically the 127 mm (5 in.) I.D. high pressure body, together with the blower and the inside return channel is called the reactor, for this experimental study only the assemblage of catalyst particles will be considered as the reactor proper. Aris (1969) pointed out the similarities between the CSTR and the catalyst particle problems. The remaining differences all vanish when the internal gradients in the catalyst particle become negligible, as was the case in our measurements. In our view the catalyst particle or particles are the reactor and the fluid flow not only supplies the reactants, but also cools the "reactor."

At the high recycle ratios and mass velocities, all gradients are minimized, therefore, in limiting case the reactor approximates well; both the isothermal and adiabatic operation. Since the temperature changes are very small, calculating a heat balance from these small temperature differences would be heavily error-laden. Therefore, to avoid these errors and those involved through the heat capacity of the system, the heat generation rate is calculated from material balance and thermochemical data. The ultimate aim is not to experiment with the thermal stability itself, but to measure

TABLE 1. COMPUTER PRINTOUT OF EXPERIMENTAL RESULTS

```
DATE:  4/9/80
TIME:  13.33 TO 15.07                                                  RUN TIME IN MINUTES = 94.00
NO. OF CYCLES:  2                                                      LIQUID COLLECTED = 27.80 GMS
                              H2            CO            CH4      CO2            H2O        CH3OH
----------------------------------------------------------------------------------------------------
FEED        [PCT
             AVG            70.478        14.548         5.883        9.091       0.          0.
             STD             0.088         0.127         0.040        0.076       0.          0.
MOLES/       RUN            11.585         2.391         0.967        1.494       0.          0.
VENT         PCT
             AVG(G)         70.843        11.786         7.008       10.018       0.058       0.345
             STD(G)          0.            0.056         0.037        0.050       0.          0.026
             AVG(L)                                                               0.113       0.887
             STD(L)                                                               0.          0.
MOLES/       RUN(G)          9.955         1.656         0.985        1.408       0.008       0.049
MOLES/       RUN(GM)*        9.776         1.626         0.967        1.382       0.008       0.048
MOLES/       RUN(L)                                                               0.103       0.811
REACTOR      CON            66.481        11.060         6.577        9.402       0.744       5.737
REACTOR     [CONM           66.407        11.048         6.569        9.391       0.755       5.829
RATE MOL/KG. HR
            [AVG           -39.275       -17.714         0.428       -2.086       2.682      20.695
             AVGM          -43.597       -18.433         0.          -2.697       2.679      20.674
             STD             0.511         0.694         0.034        0.130       0.          0.088
BAL          PCT             C             H             O         PRE   ATM      AUTO       VENT
             AVG            98.881        98.294        98.861                   52.020       1.000
             AVGM          100.391        99.868       100.366
                                                                   FLO   M/HR     FEED       VENT
TEMP         C               BED         CONDENSOR                         AVG    10.493       8.970
             IN            232.000                                         STD     0.017       0.017
            [OUT           234.000        27.000                          AVGM    10.493       8.808
```

Concentrations are in mol %. * M indicates results corrected on no change in CH_4 moles basis.

the heat generation rate and its dependence on conditions under thermally most stable operation. To increase the measurement precision, the inner, per-pass material balance is replaced by the equivalent outer overall material balance. This and other concepts were explained in a previous paper (Berty, 1979).

Experimental Procedure. Feed composition was set by Brooks regulators and measured by rotameters at 0.6 MPa (6 atm) pressure. A Haskel compressor was used to boost the pressure to 12.0 MPa (120 atm) for storage. The feed rate to the reactor was controlled by a Brooks mass flow meter-controller. The reactor was operated isothermally and with very high recycle rates and high mass velocities. Leaving the reactor, the gas was cooled, a condensate separated, drained and analyzed. The non-condensable gases were depressurized by a Grove back pressure regulator, analyzed, and metered by a wet test unit.

From the two chromatographic analyses of each phase, the reactor discharge concentration was calculated. This and the feed rate and feed concentration were the basis for material balance and rate calculations. The results of one typical experiment are shown on Figure 1, with the details given on Table 1.

Experiments were carried out at seven different temperatures with several repeats totaling 17 measurements, all made at a fixed feed composition and feed rate. Experimental conditions are shown on Table 2.

Recycle flow was calculated from the blower speed and pressure drop vs. flow relationship on the catalyst bed, (Berty 1974). The recycle flow was the basis for calculation of the heat transfer coefficient between catalyst and the gas. Some preliminary calculations have indicated that pore diffusion limitations did not significantly influence rates. The highest experimental methanol production rate of 21 mol/kg catalyst • h is in the lower industrial production range, while the lowest rate is about one order of magnitude less (ICI, 1969).

The gaseous hourly space velocity, GHSV was calculated from the make-up feed rate at STP and the catalyst occupied volume. Due to the high pressure and high RPM of the blower, very high mass velocities were achieved with the correspondingly high heat transfer coefficients in the recycle. The calculated temperature difference between catalyst and gas was less than 0.5 K. Because of the over 600:1 recycle ratio, the adiabatic temperature rise per pass was only a few tenths of K, therefore, the operation fairly well approximated ideal isothermal and completely mixed operation. In addition, the slope of the heat removal line on the van Heerden diagram is so steep that it is practically vertical, assuring unique steady state in all experiments.

Experimental Results. The chromatographic analyses were not as good as usually can be expected, due to limitations of available instruments and funds. Part of this handicap was compensated by

TABLE 2. AVERAGE EXPERIMENTAL CONDITIONS

Catalyst				
Type	Cu-based	United Catalyst T-2370		
Size	$d_p =$	$^3/_{16}$ in. ϕ, 4.76 (10^{-3})m $^3/_{16}$ in. long, 4.76 (10^{-3})m		
Bed Volume	$V =$	20 cm^3, 20$(10^{-6})m^3$		
Weight	$W =$	26.5 g, 26.5 (10^{-3}) kg		
No. of Pellets		166		
Bed ϕ		1.875 in., 47.6 (10^{-3})m		
Depth	$L =$	0.659 in., 16.7 (10^{-6})m		
Operating Conditions				
Feed Rate	=	65.7 $(10^{-6}) \pm 0.35 (10^{-6})$ m^3/s 10.55 ± 0.056 mol/h		
Feed Components, mol %	H_2	CO	CO_2	CH_4
Desired Concentration,	70.0	15:0	10.0	5.0
Actual Concentration,	69.6 ± 0.60	15.3 ± 0.44	9.5 ± 0.35	5.6 ± 0.43
Space Velocity (STP)	GHSV =	11,830 ± 60 h^{-1}, or 3.29 ± 0.018 s^{-1}		
Residence Time (Tr, Pr)	$\theta =$	9.03 s,		
Recycle Ratio		620 ± 20		
Mass Velocity	$G =$	9.2 ± 0.29, $kg/m^2 \cdot s$		
Reynolds No.	$\frac{d_p G}{\mu} =$	3,050 ± 150, $\frac{G}{a\psi\mu} = 795 \pm 40$		
Blower Speed		1500 ± 50 rpm, 30 ± 2 s^{-1}		
Operation, Pressure	$P =$	52.0 atm abs. = 5.27 MPa,		
Temperature	$T_s =$	464 to 533K, Variable,		
Heat Transfer Coefficient	$U_o =$	2630 ± 50 $W/m^2 \cdot K$.		

TABLE 3. EXPERIMENTAL RESULTS ON METHANOL SYNTHESIS

Run No.	Temp. of Gas, K	Rate of Reaction mol/kg·h H_2O	Rate of Reaction mol/kg·h CH_3OH	Percentage Conversion to CH_3OH from CO & CO_2	Rate of Heat Generation (W)	Theoretical Adiabatic Temperature Rise, K	Material Balance C	Material Balance H	Material Balance O
14-1	464.0	0.35	2.0	1.963	1.81	20.28	102.49	101.88	103.35
14-2	464.0	0.59	3.21	3.241	1.79	19.88	99.74	102.64	100.25
15-1	477.0	1.68	7.10	6.022	4.76	52.69	100.73	100.74	100.89
15-2	477.0	1.80	6.82	6.810	4.82	53.42	101.59	102.20	101.79
14-7,8	477.0	2.03	8.26	8.177	5.18	57.38	99.70	97.24	99.73
21-3	486.0	2.10	11.57	11.562	7.64	85.41	99.49	104.28	99.99
21.4	486.0	1.73	11.46	11.463	7.59	85.02	100.02	104.47	100.33
13-1	491.0	2.14	15.50	15.760	11.30	131.88	102.48	101.32	102.62
15-3	491.0	2.27	13.21	13.174	9.41	106.52	101.62	101.71	101.58
21-1	491.0	1.60	13.64	13.728	9.19	104.65	97.42	97.22	95.37
21-2	491.0	1.63	14.0	13.910	9.36	106.45	96.42	94.13	93.60
12-1	505.0	2.69	20.67	22.082	14.3	159.76	100.39	99.87	100.36
12-2	505.0	2.53	21.05	21.998	15.1	168.38	102.32	99.80	102.86
12-5	519.0	2.50	20.84	21.258	14.5	162.49	100.30	97.43	100.34
12-6	519.0	2.43	20.23	20.667	14.9	168.10	102.85	101.01	103.03
12-3	533.0	2.61	18.90	20.032	12.9	142.22	99.57	100.49	99.47
12-4	533.0	2.62	18.98	19.595	13.9	151.83	102.08	99.97	101.86

repeating experiments several times. Satisfactory results were obtained for the methanol synthesis reaction this way. Some information on the by-product, methane, formation would be very important. This reaction is even more exothermic than the methanol formation and it is not limited by equilibrium conditions, therefore, it can cause temperature runaways in methanol converters.

In these experiments, methane formation was not observed within the analytical errors. Therefore, methane was used as an internal standard in the feed and material balances were corrected on no methane formation and consumption basis. In future experiments catalyst contaminated with iron-carbonyl will be used to study the methane formation rate, because the same occurs in commercial units. No change of catalyst activity was observed during these experiments.

Experimental results are summarized in Tables 3 and 4. Figure 3 & 4 shows the experimentally measured van Heerden diagram in more detail.

Results that can be read from the van Heerden diagram are shown on Table 4. For example, at 477 K temperature, the heat generation rate is 5 watts or in temperature units it is 60 K. The tangent to the curve intersects the abscissa at 458.5 K; therefore, this $\Delta T = 18.5$ K is the maximum permissible for stability by the slope condition. Dividing the $\Delta T = 18.5$ K into the heat generation rate of 60K gives the slope condition in dimensionless form $d\bar{q}_{gen}/dT = 3.25$ (K/K). These data do not involve any assumption, therefore, the results are valid no matter what may be the mechanism or the kinetics of the process.

In Table 4 further results are shown. These involve the assumptions that 1, the difference in steady-state and equilibrium hydrogen concentration is the driving force (expressed in mol/L at T_r and P_r); and 2, the reaction is first order on this driving force.

In addition, the adiabatic temperature generation potential β that can be calculated from thermochemical data is listed there also. From these all the additional information listed in column one can be calculated by the formulas given before. These results show that the slope condition is greater than the dynamic condition, therefore, oscillations are not possible here. In the last line the dimensionless heat transfer coefficient UDa is given. This was calculated from the recycle flow and heat transfer correlation. The value of UDa is more than 2 orders of magnitude larger than the slope criterion, therefore, the system was stable at measurement conditions, in

TABLE 4. EXPERIMENTAL RESULTS

	No Assumptions Involved	
Temperature	T	477 K
Methanol Rate	r_{CH_3OH}	10.0 mol/L·h
Water Rate	r_{H_2O}	2.4 mol/L·h
Heat Gen. Rate	q_{gen}	5.0 W
	$\bar{q}_{gen}$	60.2 K
Maximum ΔT	ΔT_{max}	18.5 K
Slope Condition	$d\bar{q}_{gen}/dT$	3.25

	These Assume First Order Rate with $(C_{H_2} - C_{H_2,eq.})$ and Consider Methanol Reaction Only	
Concentration	$(C_{H_2} - C_{H_2,eq.})$	0.204 mol/L
Ad. Temp. Rise Pot.	β	1.01
Reaction Time	θ	0.00262 h
Damköhler No.	Da	0.128
Conversion	$X = Da/(1 + Da)$	0.113
$(\partial\bar{q}_{gen}/\partial T)\|_C$	$\epsilon\beta Da$	3.68
Arrhenius No.	ϵ	28.5
Energy of Activ.	E	112.6 kJ/mol
$(\partial m/\partial C)_T$	$-(1 + Da)$	−1.128
Dynamic Cond.	$\epsilon\beta Da - (1 + Da)$	2.55
Heat Transfer Coef.	UDa	760
$d\bar{q}_{rem}/dT$	$1 + UDa$	761

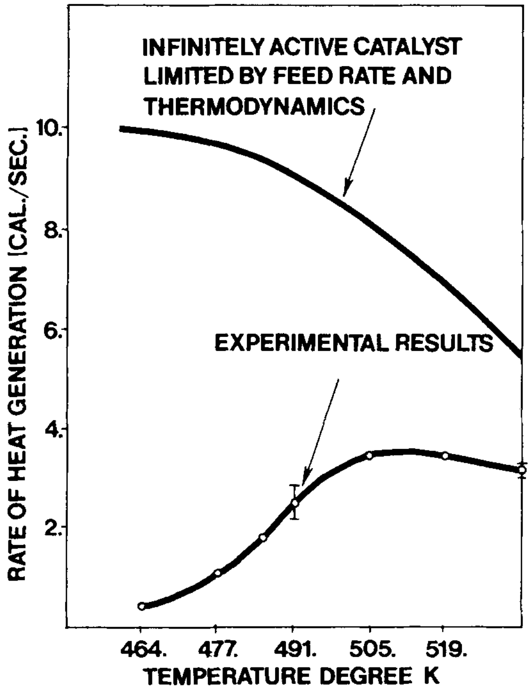

Figure 2. Heat generation rate vs. temperature in the low-pressure methanol synthesis.

essence on the scale of Figure 2, this heat removal slope would be virtually vertical.

A similar calculation for the uniqueness criterion could be attempted at the steepest part of the heat generation curve, that occurs around 496 K. Since there are few and not very good data in this region and estimating the slope would be error-prone, the calculation is not justified here.

In the industrial methanol processes, and in most industrial processes, $d\bar{q}_{rem}/dT$ will be in the high values used here. Therefore, temperature runaway will be seldom caused by poor heat transfer between catalyst and reacting gas; it will be caused in tubular reactors most likely due to inadequate heat transfer area at the tube wall. Nevertheless, measurements made the way proposed here are independent of the experimental reactor, and the results will supply the basic information for a thermally stable design. On the other hand, oscillating conditions will be possible only at very poor heat transfer rates occuring mostly in some laboratory reactors and will remain mainly interesting laboratory phenomena that can help to test theoretical conclusions.

The Damköhler number was calculated from the methanol rate alone by dividing it with hydrogen concentration difference and multiplied by the reaction time. With multiple reactions in nonstoichiometric mixtures, β can be calculated on the basis of the difference of all the heats of formation of materials at steady-state and at thermodynamic equilibrium. This β and T_s divided into the heat generation rate gives:

$$\frac{\bar{q}_{gen}}{\beta T_s} = Da.$$

In these experiments, taking in account the methanol equilibrium only, the calculated Da is the same as that from the methanol reaction. In cases where methane formation or complete decomposition is possible, an ultimate thermodynamic equilibrium calculation like those in the NASA program (Zelenik, 1962) is advisable for estimating β.

ACKNOWLEDGMENT

The authors are grateful to Autoclave Engineers, Inc. for donating the equipment; to United Catalyst, Inc. for supplying the catalyst; and to the Chemical Engineering Department of the University of Akron for financial support.

NOTATION

a = heat transfer area per reactor volume or per catalyst particle
C = concentration
c = heat capacity
Da = Damköhler number, dimensionless reaction time, $k\theta$
E = activation energy
ΔH_r = heat of reaction
k = kinetic constant
k_o = pre-exponential factor
m = mass balance function
n = order of reaction
q = heat generation rate
$\bar{q}$ = heat rate, in temperature dimension
Q = feed rate
r = rate of reaction
R = gas constant
T = temperature
U = time constant ratio = $U_o a/\rho c\, k_s$
U_o = overall heat transfer coefficient
UDa = dimensionless heat transfer coefficient $U_o a\theta/\rho c$
V = reactor volume
X = fractional conversion

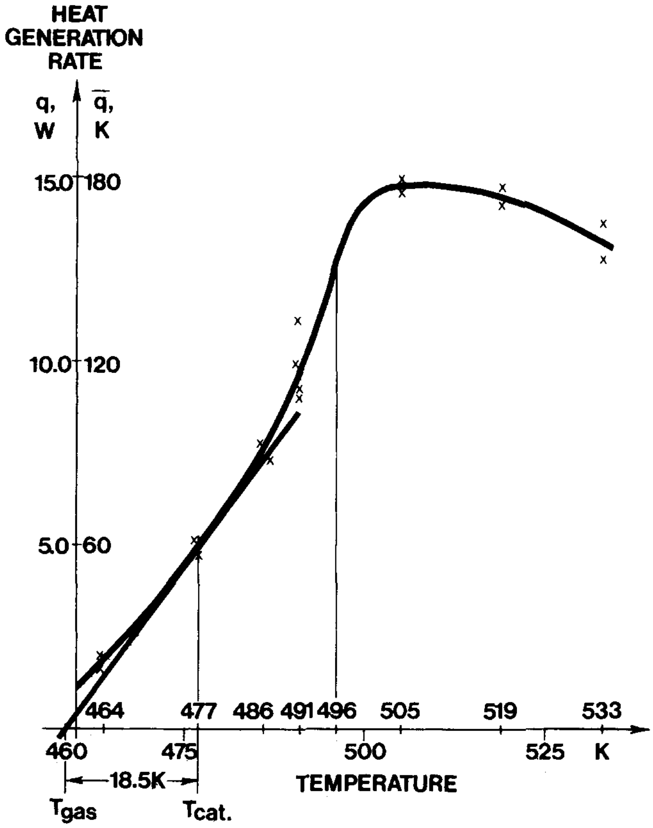

Figure 3. Experimentally measured van Heerden diagram for the low-pressure methanol synthesis.

Greek Letters

β = dimensionless temperature rise potential = $(-\Delta H)C_s/\rho c T_s$
ϵ = Arrhenius no. = E/RT_s
θ = reaction time = V/Q
ρ = density

Subscripts

o = feed
s = steady state
gen = generated
tr = transferred
ad = adiabatic
rem = removal

LITERATURE CITED

Aris, R., and N. R. Amundson, "An Analysis of Chemical Reactor Stability and Control—I," *Chem. Eng. Sci.*, **7**, 121 (1958).

Aris, R., "On Stability Criteria of Chemical Reaction Engineering," *Chem. Eng. Sci.*, **24**, 149 (1969).

Berty, J. M., "Stability of Staged Adiabatic Reactors with Interstage Coolers," Preprint No. 10E, 63rd National Meeting of AIChE, St. Louis, MO (Feb. 18-21, 1968).

Berty, J. M., J. O. Hambrick, T. R. Malone, and D. S. Ullock, "Reactor for Vapor-phase Catalytic Studies," Paper No. 42, 64th Nat. Meeting of AIChE, New Orleans, LA (1969).

Berty, J. M., "Reactor for Vapor-Phase Catalytic Studies," *Chem. Eng. Prog.*, **70**, 78 (1974).

Berty, J. M., "Testing Commercial Catalysts in Recycle Reactors," *Catal. Rev.—Sci. Eng.*, **20**, 1, 75 (1979).

Bush, S. F., "The Measurement and Prediction of Sustained Temperature Oscillations in a Chemical Reactor," Proc. Roy. Soc. A. 309, 1-26 (1964).

Bush, S. F., "The Measurement and Prediction of Instability in Certain Exothermic Vapor-phase Reactors," *Advances in Chemistry Series*, **104**, 610 (1972).

Cappelli, A., and M. Dente, "Application of a Nonlinear Evaluation Method to the Analysis of Kinetic Data from an Integral Reactor," *Chim. E. Ind.*, **47**, 1068 (1965).

Carberry, J. J., "Chemical and Catalytic Reaction Engineering," McGraw-Hill (1976).

Carra, S., and L. Forni, "Aspetti Cinetici delta Teoria del Reatore-Chimico," Tamburini, Milan (1974).

Cropley, J. B., "Heuristic Approach to Complex Kinetics," *ACS Symp. Ser.*, **65**, 292 (1978).

Damköhler, G., "Einflüsse der Strömung, Diffusion und des Wärmeüberganges auf die Leistung von Reaktionsofen," *Z. Elektrochem.*, **42**, No. 12, 846 (1936).

Damköhler, G., *Der Chemie—Ingenieur* **III**, Part One, 447 (1937).

Frank-Kamenetskii, D. A., "Ignition of Coal and High-Speed Gasification," *J. Tech. Phys.*, (USSR) **9**, 1457 (1939).

Frank-Kamenetskii, D. A., "Diffusion and Heat Transfer in Chemical Kinetics," Plenum Press, 2nd ed. (1961).

Froment, G. E., and K. B. Bischoff, "Chemical Reactor Analysis and Design," John Wiley (1976).

Gilles, E. D., and H. Hofmann, "Bermerkung zu der Arbeit: An Analysis of Chemical Reactor Stability and Control," *Chem. Eng. Sci.*, **5**, 328 (1961).

ICI, "Low-Cost, Low-Pressure Methanol," *Chem. Eng.*, 86 (Dec. 1, 1969).

Kung, H. H., "Methanol Synthesis," *Catal. Rev.—Sci. Eng.*, **22** (2), 235 (1980).

Liljenroth, F. G., "Starting and Stability Phenomena of Ammonia-Oxidation and Similar Reactions," *Chem. Met. Eng.*, **19**, 287 (1918).

Luss, D., Professional Progress Award Lecture, 73rd Annual Meeting of AIChE, Chicago, IL (Nov. 10–20, 1980).

Natta, G., "Synthesis of Methanol," *Catalysis*, P. H. Emmett, ed., **3**, 345, Reinhold, NY (1955).

Parekh, V. J., "Preliminary Kinetic Study of the Low-Pressure Methanol Synthesis," M.S. Thesis, Univ. of Akron, Akron, OH (1980).

Perkins, G. A., Carbide and Carbon Chemical Corp., Weekly Progress Report 3/15 (1938).

Perlmutter, D. D., "Stability of Chemical Reactors," Prentice-Hall, Inc. (1972).

Schmitz, R. A., "Multiplicity, Stability and Sensitivity of States in Chemically Reacting Systems—A Review," *Advances in Chemistry Series*, **148**, Chem. Reaction Eng. Reviews (1975).

Schmitz, R. A., R. R. Bautz, W. E. Ray, and A. Uppal, "The Dynamic Behavior of a CSTR: Some Comparisons of Theory and Experiment," *AIChE J.*, **25**, No. 2, 289 (March 1979).

Shinnar, R., "Chemical Reactor Modeling—The Desirable and the Achievable," *ACS Symp. Ser.* No. 72 (1978).

Stephens, A. D., "Stability and Optimization of a Methanol Converter," *Chem. Eng. Sci.*, **30**, 11 (1975).

Uppal, A., W. H. Ray, and A. B. Poore, "On the Dynamic Behavior of Continuous Stirred Tank Reactors," *Chem. Eng. Sci.*, **29**, 967 (1974).

Uppal, A., W. H. Ray, and A. B. Poore, "The Classification of the Dynamic Behavior of Continuous Stirred Tank Reactors—Influence of Reactor Residence Time," **31**, 205 (1976).

Van Heerden, C., "Autothermic Processes—Properties and Reactor Design," *Ind. Eng. Chem.*, **45**, 1242 (1953).

Van Heerden, C., "The Character of the Stationary State of Exothermic Processes," Proc. of the 1st European Symposium on Chemical Reaction Engineering, p. 133, Amsterdam, Pergamon Press (1958).

Wagner, C., "Über die Temperature Einstellung an Hochstleistungskatalysatoren," *Chem. Tech.*, **18**, 28 (1945).

Weller, S. W., "Kinetic Models in Heterogeneous Catalysis," *Adv. in Chem. Ser.*, No. 148 (1976).

Wicke, E., and D. Vortmeyer, "Zündzonen heterogener Reaktionen in gasdurchströmten Körnerschichten," Z. *für Elektrochemie*, **63**, 145 (1959).

Wilson, K. B., "Tubular Reactors-Calculation and Analysis of Longitudinal Temperature Gradients in Tubular Reactors," *Trans. Inst. Chem. Eng.*, **24**, 77 (1946).

Zelenik, F. G., and S. Golden, "A General IBM 704 or 7090 Computer Program for Computation of Chemical Equilibrium Composition, Rocket Performance, and Chapman-Jouquet Detonations," NASA Technical Note, D-1454 (1962).

Manuscript received March 30, 1981; revision received December 17, and accepted January 13, 1982.

Time Dependence of Pressure In a Bubbler Tube

A. K. GAIGALAS
and
BALDWIN ROBERTSON

Fluid Engineering Division
National Bureau of Standards
Washington, DC 20234

An experimental and theoretical study is presented of the time dependence of air pressure in a bubbler tube used to measure the liquid level in a tank. The observed time dependence of the air pressure is a superposition of two components. The first component is a repeated slow rise and sudden fall in the air pressure that is associated with bubble growth and breakoff. It is the sudden breakoff that generates the second component consisting of damped oscillations associated with sound waves in the air interacting with an oscillating flow of the liquid. The air pressure during bubble growth is described theoretically. This result is combined with the gas law to predict the functional form of the slow pressure rise; this prediction agrees with experiment. An equation for the oscillation frequencies is derived, solved, and compared with experiment; agreement is within the measurement accuracy of 5%.

SCOPE

A widespread method for measuring the level of liquid contained in a tank uses a tube inserted down into the liquid and through which air (or nitrogen) is forced under pressure. The method is used in industry where a pressure transducer cannot be put inside the tank. Since the pressure necessary to force the air out of the lower end of the tube depends on the height of the liquid above the end of the tube, a measurement of the air pressure can be used to infer the height of the liquid. This can be used to determine the volume of liquid in the tank if the cross

---

Correspondence concerning this paper should be addressed to A. K. Gaigalas.

0001-1541-82-6525-0922-$2.00.