

CHEMICAL ENGINEERING KINETICS
Second Edition

INTRODUCTION

The design and operation of equipment for carrying out chemical reactions require analysis of both physical and chemical processes. The principles governing energy and mass transfer are often as important as those which govern chemical kinetics. This combination of physical and chemical operations is also a distinguishing feature of chemical engineering; the design of chemical reactors is an activity unique to the chemical engineer.

In designing a reactor the following factors must be considered: the type and size needed, provisions for exchange of energy (usually as heat) with the surroundings, and operating conditions (temperature, pressure, composition, flow rates). We identify this problem as the *process design* of the reactor. A cost analysis to determine the most profitable design introduces further questions about construction materials, corrosion, utility requirements, and maintenance. In order to maximize profits, the instrumentation and a control policy (ranging from manual to closed-loop computer control) for optimum operation must be determined. Optimum design will also depend indirectly on estimates of such market conditions as the price-volume relationships for reactants and products. While these factors are important in overall design and operation of reactors, they will

not be discussed in this book. Our use of the term *design* will be restricted to *process design*.

The rate of transforming one chemical species into another cannot be predicted with accuracy. It is a specific quantity which must be obtained from experimental measurements. Measuring the *rate of chemical reactions* is the art and science of chemical kinetics (to be discussed in Sec. 1-3). Chemical kinetics is not concerned with physical processes, but only with the rate of transformation of atoms and molecules from one structural form to another. In contrast, the rates of physical processes such as heat and mass transfer can in many types of reactors be estimated reliably from the flow and geometrical arrangements. Hence it is desirable to consider the design of *types of reactors*, rather than approach each chemical system as a separate entity. Because of the specific nature of chemical processes, this generalization is not as successful as it would be, say, for designing heat exchangers. However, some conclusions are possible for reactors, because the kinetics of chemical reactions of a given type, such as homogeneous gas phase or gas-solid catalytic, have similarities.

Our chief objective is to determine how to answer process-design questions for various types of chemical reactions and reactors.

1-1 Interpretation of Rate Data, Scale-up, and Design

The chemical engineer depends on data from the chemist's laboratory, the pilot plant, or a large-scale reactor to help him in his design work. From this information he needs to extract, among other things, the rates of the chemical reactions involved, i.e., the chemical kinetics of the system. To do this he must separate the effects of physical processes from the observed data, leaving rate information for the chemical-transformation step alone. He can then reintroduce the influence of the physical steps for the particular reactor type and operating conditions chosen for the commercial plant. The interrelationship of the physical and chemical steps must be considered twice: once in obtaining rate-of-reaction expressions from the available laboratory or pilot-plant data, and again in using these rate-of-reaction equations to design the commercial-scale reactor. The first step, interpretation of the available data, is as important as the second and entails generally the same type of analysis. Hence the interpretation of laboratory data will sometimes be discussed in parallel with the reactor-design problem in the chapters that follow. Interpreting laboratory-reactor data is not necessarily as difficult and does not always entail the same steps (in reverse order) as reactor design. Because there are fewer restraints (economic ones, for example), there is more flexibility in choosing a laboratory reactor. It is common practice to design a laboratory reactor to minimize the signif-

icance of physical processes (see Chap. 12). This eliminates the need for accurate separation of physical and chemical effects and produces more accurate results for the rates of the chemical steps. For instance, a laboratory reactor may be operated at near-isothermal conditions, eliminating heat-transfer considerations, while such operation would be uneconomical in a commercial-scale system.

It is important to consider the relationship between reactor *scale-up* (projection of laboratory or pilot-plant data to the commercial reactor) and reactor design. In principle, if the rates of the chemical reactions are known, any type of reactor may be designed by introducing the appropriate physical processes associated with that type of equipment. Scale-up is an abbreviated version of this design process. The physical resistances are not separated from the measured laboratory data but are instead projected directly to a large unit which presumably has the same interrelationship of chemical and physical processes. If the dimensions and operating conditions for the large-scale reactor can be determined to ensure that the interrelationships of chemical and physical processes are the same as in the laboratory unit, then the laboratory results may be used directly to predict the behavior of the large-scale reactor. In a scale-up process no attempt is made to determine the rate of the chemical steps, that is, to evaluate the chemical kinetics of the process. However, when scale-up is applicable, it provides a rapid means of obtaining approximate reactor sizes, and also indicates the important parameters in the interrelationship between physical and chemical processes (see Sec. 12-5).

Scale-up will have a much better chance for success if the laboratory and commercial operations are carried out in the same type of system. Suppose that laboratory data for the thermal cracking of hydrocarbons are obtained in a continuous tube through which the reaction mixture flows. If a tubular-flow reactor of this type is also proposed for the commercial plant, it may be possible to scale-up the pilot-plant operation in such a way that the temperature and concentration gradients within the tube will be the same in both systems. Then performance of the large-scale reactor—for example, conversion of reactants to various products—can be predicted directly from the laboratory results. However, if the laboratory results were obtained from a batch reactor, a tank or vessel into which the reactants are initially charged (see Sec. 1-6), it is difficult to project them directly to a large-scale tubular reactor. In this case it would be necessary to analyze the laboratory data to obtain the rate equation for the chemical reactions and then use these results to design the commercial reactor. Our emphasis will be on this two-step process of determining the rates of reaction from laboratory data and then using these rates for design.

The foregoing comments do not imply that pilot-plant data from a

small-scale replica of a proposed commercial unit are of no value. Such information provides an important evaluation of both the laboratory rate data and the procedures used to reintroduce the physical processes in the pilot reactor and, presumably, in the final equipment.

Our discussion thus far of the interrelationship of chemical and physical processes in a reactor has been general. Let us look further into the problem by considering a very simple reaction system, the conversion of ortho hydrogen to the para form.¹ Owing to thermodynamic restrictions (see Sec. 1-5), this reaction must be carried out at a low temperature in order to obtain a large conversion to para hydrogen. At low temperatures it is necessary to use a catalyst to obtain a rapid rate of reaction. The preferred type of reactor is a continuous steady-state system in which hydrogen flows through a tube packed with pellets of the solid catalyst. Consider the interpretation of rate measurements made with a laboratory version of this type of reactor. The observed data would consist of measurements of hydrogen compositions in the inlet and exit streams of the reactor. Probable variables would be the flow rate of hydrogen through the reactor, the mole fraction of para hydrogen in the feed to the reactor, and the temperature. The heat of reaction is negligible, so that the whole reactor system can easily be operated at isothermal conditions.

The first problem in designing a reactor for the production of para hydrogen is to obtain from the observed measurements a quantitative expression for the rate of reaction on the surface of the catalyst. Specifically, we must separate from the observed data the diffusional resistances between the point at which the composition is measured—the exit of the reactor—and the point at which the chemical transformation occurs—the gas-solid interface at the catalyst surface. There are three diffusional effects that may cause a difference between the conversion measured in the exit of the reactor and that predicted from the rate at the catalyst interface. The first arises from the mixing characteristics of the fluid as it flows around the particles in the fixed bed. There may be some bypassing or short circuiting, so that part of the flowstream does not come into contact with the catalyst; also, there may be diffusion or back-mixing of fluid as it flows through the bed. As a result, the observed amount of para hydrogen in the exit gas may be less than expected. The second factor is the tendency of the fluid to adhere to the catalyst pellet, so that the pellet is surrounded by a more or less stagnant layer of fluid which resists mass transfer. Thus a concentration gradient of para hydrogen must be established between the outer surface of the pellet and the bulk gas before the para hydrogen will

¹This reactor-design problem has some practical significance because of the superior storage properties of liquid hydrogen when it is in the para form. Noriaki Wakao and J. M. Smith, *AIChE J.*, 8, 478 (1962).

move on into the gas stream. This reduces the amount of para hydrogen available to the bulk-gas phase. A third factor is that most of the active surface of the catalyst is in the pores within the pellet. The reactant must reach this interior pore surface by diffusing into the pellet, and the product must diffuse out. This process is impeded by intraparticle resistance, causing another reduction in the para-hydrogen content of the gas stream. Thus to determine the rate of reaction on the surface of the catalyst (the chemical kinetics of the process) it is necessary to evaluate the concentration changes for each of these diffusional effects, ultimately arriving at the concentration of para hydrogen in the interior pore surface of the catalyst pellet. The interior concentration can then be used to establish a rate-of-reaction equation.

The second problem is use of the rate equation to design a commercial reactor. The individual diffusional resistances are now reintroduced so that we may determine the actual composition of para hydrogen in the exit stream from the reactor. Once the equation for the surface rate is known, it is possible, in principle, to predict the exit conversion for any type of reactor, any size catalyst pellet, any conditions of gas flow around the pellet, and any condition of mixing of fluid around the particles in the fixed bed.

If the same problem were approached from a scale-up standpoint, the procedure would be to attempt to choose the operating conditions and reactor size for the large-scale reactor such that the diffusional resistances were the same as in the laboratory equipment.

1-2 Principles of Chemical-reactor Design

Now that we have discussed briefly the problems in chemical-reactor design, let us explore the concepts necessary to solve these problems.¹ First, we must know something about the formulation of equations for the rate of chemical transformation from one species to another. This is the subject of chemical kinetics. While we cannot predict the rate of a chemical reaction, chemical kineticists have developed a number of valuable generalizations for formulating rate equations. It is necessary to understand these generalizations before proceeding with the design problem. Also, the rate equation must account for the thermodynamic limitations on the chemical reaction. For example, the ortho-para hydrogen conversion is a reaction in which the maximum conversion is less than 100%. An understanding of the equilibrium conversion as a function of operating conditions is necessary before a satisfactory rate equation can be formed. Thermodynamics also

¹R. Aris [*Ind. Eng. Chem.*, 56, 22 (1964)] and J. M. Smith [*Chem. Eng. Progr.*, 64, 78 (1968)] have shown how physical and chemical sciences play a role in the design, analysis, and control of reactors.

comes into play in evaluating energy transfer in the reactor. Hence a primary requisite is a knowledge of chemical thermodynamics (Sec. 1-5).

Along with kinetics, the engineering concepts required to evaluate the conversion in the product from a reactor are of two types: the principles of conservation of mass and energy and rate equations for the physical processes. The conservation of mass and the rate of mass transfer determine the composition as a function of position in a continuous reactor and as a function of time in a batch reactor. Similarly, the conservation of energy and the rate of energy transfer determine the temperature as a function of position or time. The application of these principles is discussed in subsequent chapters, starting with Chap. 3 where mathematical formulations are considered for various types of reactors.

1-3 Chemical Kinetics

Chemical kinetics is the study of the rate and mechanism by which one chemical species is converted to another. The *rate* is the mass, in moles, of a product produced or reactant consumed per unit time. The *mechanism* is the sequence of individual chemical events whose overall result produce the observed reaction. Basolo and Pearson¹ have described the term "mechanism" as follows:

By mechanism is meant all the individual collisional or elementary processes involving molecules (atoms, radicals and ions included) that take place simultaneously or consecutively in producing the observed overall rate. It is also understood that the mechanism of a reaction should give a detailed stereochemical picture of each step as it occurs. This implies a knowledge of the so-called activated complex or transition state, not only in terms of the constituent molecules but also in terms of the geometry, such as interatomic distances and angles. In most instances the postulated mechanism is a theory devised to explain the end results observed by experiments. Like other theories, mechanisms are subject to change over the years as new data is uncovered or as new concepts regarding chemical interreactions are developed.

It is not necessary to know the mechanism of a reaction in order to design a reactor. What is necessary is a satisfactory rate equation. A knowledge of the mechanism is of great value, however, in extending the rate data beyond the original experiments and in generalizing or systematizing the kinetics of reactions. Determining the mechanism of a reaction is a very difficult task and may require the work of many investigators over a period of many years. Reaction mechanisms are reliably known for only a

¹F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, 1958.

few systems. However, postulated theories for mechanisms are available for a wide variety of reactions, ranging from simple, gas-phase homogeneous systems to complicated polymerization reactions involving initiation, propagation, and termination steps.

Since reactor design necessitates a reliable rate equation, this aspect of chemical kinetics is presented in detail in Chap. 2. Successful procedures for *predicting* rates of reactions will not be developed until reaction mechanisms are better understood. It is important for those involved in reactor design to be aware of developments in this area so that they may take advantage of new principles of chemical kinetics as they are developed. A brief discussion of theories of reaction and mechanisms is included in Chap. 2.

The rate of a chemical reaction can vary from a value approaching infinity to essentially zero. In ionic reactions, such as those that occur on photographic film, or in high-temperature combustion reactions, the rate is extremely fast. The rate of combination of hydrogen and oxygen in the absence of a catalyst at room temperature is immeasurably slow. Most industrially important reactions occur at rates between these extremes, and it is in these cases that the designer must apply data on kinetics to determine finite sizes of reaction equipment. It is particularly important to know how the rate changes with operating parameters, the most important of which are temperature, pressure, and composition of reaction mixture.

The science of kinetics is young. The first quantitative measurements of reaction rates were made in the middle of the nineteenth century by Wilhelmly,¹ Berthelot and St. Gilles,² and Harcourt and Esson.³ The first attempt to develop a theory explaining the manner in which molecules of a substance react was that of Arrhenius⁴ in 1889. He postulated that the reactants had both inert and active molecules and that only the active ones possessed sufficient energy to take part in the reaction. Since these early developments there have been a great many experimental studies of reaction rates for a wide variety of reactions, but few noteworthy advances in theory were made until the work of Eyring and Polanyi,⁵ beginning in 1920. Using only such fundamental information as the configurations, dimensions, and interatomic forces of the reacting molecules, they postulated an activated-complex theory for predicting the rate of reaction. Lack of exact knowledge of the interatomic forces, and hence of energy-position relations, for any but the most simple molecules has prevented the activated-complex theory

¹L. Wilhelmly, *Pogg. Ann.*, **81**, 413, 499 (1850).

²M. Berthelot and L. P. St. Gilles, *Ann. Chim. Phys.*, **63** (3), 385 (1862).

³A. V. Harcourt and W. Esson, *Proc. Roy. Soc. (London)*, **14**, 470 (1865).

⁴S. Arrhenius, *Z. Physik Chem.*, **4**, 226 (1889).

⁵H. Eyring and M. Polanyi, *Z. Physik Chem. B*, **12**, 279 (1931).

from being useful for predicting reaction-rate data accurately enough for engineering work. While these theoretical developments have been of great value in the search for an understanding of how and why a chemical reaction takes place, the quantitative evaluation of the rate remains an experimental problem.

The large amount of experimental data on rates of chemical reaction have established reliable empirical forms for the mathematical expression of the effects of such variables as temperature and composition on the rate. These results are interpreted for various types of reactions in Chap. 2.

1-4 Kinetics and Thermodynamics

From the principles of thermodynamics and certain thermodynamic data the maximum extent to which a chemical reaction can proceed may be calculated. For example, at 1 atm pressure and a temperature of 680°C, starting with 1 mole of sulfur dioxide and $\frac{1}{2}$ mole of oxygen, 50% of the sulfur dioxide can be converted to sulfur trioxide. Such thermodynamic calculations result in maximum values for the conversion of a chemical reaction, since they are correct only for equilibrium conditions, conditions such that there is no further tendency for change with respect to time. It follows that the net rate of a chemical reaction must be zero at this equilibrium point. Thus a plot of reaction rate [for example, in units of g moles product/(sec) (unit volume reaction mixture)] vs time would always approach zero as the time approached infinity. Such a situation is depicted in curve *A* of Fig. 1-1, where the rate approaches zero asymptotically. Of course, for some cases equilibrium may be reached more rapidly, so that the rate becomes almost zero at a finite time, as illustrated by curve *B*.

Similarly, the *conversion* (fraction of reactant transformed or converted) calculated from thermodynamic data would be the end point on a curve of conversion vs time such as that shown in Fig. 1-2. Again, curve *A* represents the case where the time required to reach equilibrium conditions is great, while in case *B* the equilibrium conversion is approached more rapidly and is attained essentially at a finite time. Curves *A* and *B* could apply to the same reaction; the difference between them reflects the fact that in case *B* the rate has been increased, for example, by use of a catalyst. The rate of the reaction is initially increased over that for the uncatalyzed reaction, but the equilibrium conversion as shown in Fig. 1-2 is the same for both cases.

The time available for carrying out a chemical reaction commercially is limited if the process is to be economically feasible. Hence the practical range of the curves in Figs. 1-1 and 1-2 is at the lower time values. However, the equilibrium conversion is important as a standard for evaluating the actual performance of the reaction equipment. Suppose a kinetics experi-

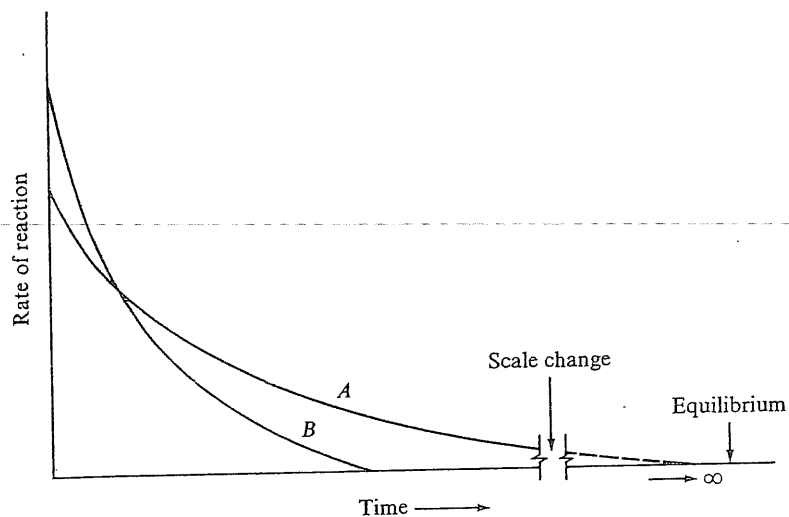
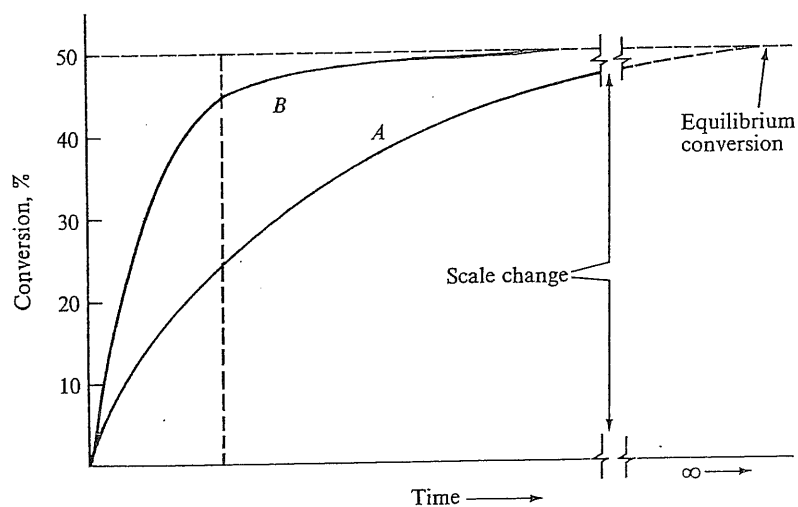


Fig. 1-1 Rate of reaction vs time

ment is carried out with a time corresponding to the dashed vertical line shown in Fig. 1-2. At this point the conversion for the noncatalytic reaction is about 25% (curve A). A comparison with the equilibrium value of 50% indicates that the noncatalytic rate is rather low and that a search for a catalyst is advisable. Curve B, giving a conversion of 45%, shows the benefit of using a catalyst and also indicates that additional effort to find a more

Fig. 1-2 Conversion vs time



effective catalyst is unwarranted. Without prior knowledge of the equilibrium conversion, erroneous conclusions might well be drawn from the kinetic studies yielding curves *A* and *B*. For example, it might be reasoned that the catalyst giving curve *B* is only moderately effective, and considerable time might be spent in attempting to discover a catalyst which would give a conversion of 70 or 80%. Thermodynamic calculations are particularly valuable for such comparison of kinetic and equilibrium results. However, the actual design of reactors usually depends on the location of the curves shown in Figs. 1-1 and 1-2 and must therefore be determined by kinetic studies.

Prediction of the equilibrium conversion requires knowledge of the free-energy change for the reactions involved. Although the body of thermodynamic data is growing, it is still not possible to estimate the equilibrium conversion accurately for all reactions. The calculations and data available for gaseous systems are most reliable. The application of thermodynamics for such calculations is illustrated very briefly in the following section. More detailed treatment of the thermodynamics of chemical-reaction equilibrium is given in thermodynamics textbooks.¹

The rate of energy transfer is important in determining the temperature distribution in reactors. Also, heats of reaction are significant in connection with equilibrium calculations. The following section deals with data and methods concerning heats of reaction, followed by a discussion of equilibrium conversion.

1-5 Thermodynamics of Chemical Reactions

Heat of Reaction The *heat of reaction* is defined as the energy absorbed by the system when the products after reaction are restored to the same temperature as the reactants. The pressure must also be specified for a complete definition of the thermodynamic states of the products and reactants. If the same pressure is chosen for both, the heat of reaction is equal to the enthalpy change; this is the customary definition of the heat of reaction. The heat of any reaction can be calculated by combining heats of formation or heats of combustion of the products and reactants. Thus the basic information necessary for calculating heats of reaction are heats of formation and

¹B. F. Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, New York, 1944; J. G. Kirkwood and Irwin Oppenheim, "Chemical Thermodynamics," McGraw-Hill Book Company, New York, 1961; G. N. Lewis and M. Randall, "Thermodynamics," 2d ed., rev. by K. S. Pitzer and Leo Brewer, McGraw-Hill Book Company, New York, 1961; J. M. Smith and H. C. Van Ness, "Introduction to Chemical Engineering Thermodynamics," McGraw-Hill Book Company, New York, 1959; H. C. Van Ness, "Classical Thermodynamics of Non-electrolyte Solutions," The Macmillan Company, Inc., New York, 1964.

Table 1-1 Standard heats of formation and combustion for reaction products $H_2O(l)$ and $CO_2(g)$ at $25^\circ C$, in calories per gram mole

Substance	Formula	State	$\Delta H_{f,298}^\circ$	$-\Delta H_{c,298}^\circ$
Normal paraffins				
Methane	CH_4	<i>g</i>	-17,889	212,800
Ethane	C_2H_6	<i>g</i>	-20,236	372,820
Propane	C_3H_8	<i>g</i>	-24,820	530,600
<i>n</i> -Butane	C_4H_{10}	<i>g</i>	-30,150	687,640
<i>n</i> -Pentane	C_5H_{12}	<i>g</i>	-35,000	845,160
<i>n</i> -Hexane	C_6H_{14}	<i>g</i>	-39,960	1,002,570
Increment per C atom above C_6	...	<i>g</i>	-4,925	157,440
Normal monoolefins (1-alkenes)				
Ethylene	C_2H_4	<i>g</i>	12,496	337,230
Propylene	C_3H_6	<i>g</i>	4,879	491,990
1-Butene	C_4H_8	<i>g</i>	-30	649,450
1-Pentene	C_5H_{10}	<i>g</i>	-5,000	806,850
1-Hexene	C_6H_{12}	<i>g</i>	-9,960	964,260
Increment per C atom above C_6	...	<i>g</i>	-4,925	157,440
Miscellaneous organic compounds				
Acetaldehyde	C_2H_4O	<i>g</i>	-39,760	
Acetic acid	$C_2H_4O_2$	<i>l</i>	-116,400	
Acetylene	C_2H_2	<i>g</i>	54,194	310,620
Benzene	C_6H_6	<i>g</i>	19,820	789,080
Benzene	C_6H_6	<i>l</i>	11,720	780,980
1,3-Butadiene	C_4H_6	<i>g</i>	26,330	607,490
Cyclohexane	C_6H_{12}	<i>g</i>	-29,430	944,790
Cyclohexane	C_6H_{12}	<i>l</i>	-37,340	936,880
Ethanol	C_2H_6O	<i>g</i>	-56,240	
Ethanol	C_2H_6O	<i>l</i>	-66,356	
Ethylbenzene	C_8H_{10}	<i>g</i>	7,120	1,101,120
Ethylene glycol	$C_2H_6O_2$	<i>l</i>	-108,580	
Ethylene oxide	C_2H_4O	<i>g</i>	-12,190	
Methanol	CH_4O	<i>g</i>	-48,100	
Methanol	CH_4O	<i>l</i>	-57,036	
Methylcyclohexane	C_7H_{14}	<i>g</i>	-36,990	1,099,590
Methylcyclohexane	C_7H_{14}	<i>l</i>	-45,450	1,091,130
Styrene	C_8H_8	<i>g</i>	35,220	1,060,900
Toluene	C_7H_8	<i>g</i>	11,950	943,580
Toluene	C_7H_8	<i>l</i>	2,870	934,500
Miscellaneous inorganic compounds				
Ammonia	NH_3	<i>g</i>	-11,040	
Calcium carbide	CaC_2	<i>s</i>	-15,000	
Calcium carbonate	$CaCO_3$	<i>s</i>	-288,450	
Calcium chloride	$CaCl_2$	<i>s</i>	-190,000	
Calcium chloride	$CaCl_2 \cdot 6H_2O$	<i>s</i>	-623,150	
Calcium hydroxide	$Ca(OH)_2$	<i>s</i>	-235,800	
Calcium oxide	CaO	<i>s</i>	-151,900	

Table 1-1 (Continued)

Substance	Formula	State	$\Delta H_f^\circ_{298}$	$-\Delta H_c^\circ_{298}$
Carbon	C	Graphite	...	94,052
Carbon dioxide	CO ₂	<i>g</i>	-94,052	
Carbon monoxide	CO	<i>g</i>	-26,416	67,636
Hydrochloric acid	HCl	<i>g</i>	-22,063	
Hydrogen	H ₂	<i>g</i>	...	68,317
Hydrogen sulfide	H ₂ S	<i>g</i>	-4,815	
Iron oxide	FeO	<i>s</i>	-64,300	
Iron oxide	Fe ₃ O ₄	<i>s</i>	-267,000	
Iron oxide	Fe ₂ O ₃	<i>s</i>	-196,500	
Iron sulfide	FeS ₂	<i>s</i>	-42,520	
Lithium chloride	LiCl	<i>s</i>	-97,700	
Lithium chloride	LiCl · H ₂ O	<i>s</i>	-170,310	
Lithium chloride	LiCl · 2H ₂ O	<i>s</i>	-242,100	
Lithium chloride	LiCl · 3H ₂ O	<i>s</i>	-313,500	
Nitric acid	HNO ₃	<i>l</i>	-41,404	
Nitrogen oxides	NO	<i>g</i>	21,600	
	NO ₂	<i>g</i>	8,041	
	N ₂ O	<i>g</i>	19,490	
	N ₂ O ₄	<i>g</i>	2,309	
	Na ₂ CO ₃	<i>s</i>	-270,300	
Sodium carbonate	Na ₂ CO ₃ · 10H ₂ O	<i>s</i>	-975,600	
Sodium chloride	NaCl	<i>s</i>	-98,232	
Sodium hydroxide	NaOH	<i>s</i>	-101,990	
Sulfur dioxide	SO ₂	<i>g</i>	-70,960	
Sulfur trioxide	SO ₃	<i>g</i>	-94,450	
Sulfur trioxide	SO ₃	<i>l</i>	-104,800	
Sulfuric acid	H ₂ SO ₄	<i>l</i>	-193,910	
Water	H ₂ O	<i>g</i>	-57,798	
Water	H ₂ O	<i>l</i>	-68,317	

SOURCE: Most values have been selected from the publications of F. D. Rossini et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, *Am. Petrol. Inst. Res. Proj. 44*, Carnegie Institute of Technology, Pittsburgh, 1953; F. D. Rossini et al., Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Stds. Circ. 500*, 1952.

combustion. Extensive tables of these data have been accumulated,¹ and a few values are summarized in Table 1-1.

¹Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Stds. Circ. 500*, 1952; Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, *Am. Petrol. Inst. Res. Proj. 44*, Carnegie Institute of Technology, Pittsburgh, 1953.

In the absence of experimental data, there are procedures available for predicting heats of reaction.¹ These are all based on predictions of the effects of differences in the chemical structure of the reactants and products. One of the most useful procedures from an engineering standpoint is that proposed by Andersen et al. and described in detail by Hougen and Watson.² This method is applicable to compounds involving carbon, hydrogen, oxygen, nitrogen, and the halogens.

The variation of heat of reaction with temperature depends on the difference in molal heat capacities of the products and reactants. The following equation relates ΔH at any temperature T to the known value at the base temperature T_0 :

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T \Delta C_p dT \quad (1-1)$$

Here ΔC_p is the difference in molal heat capacities,

$$\Delta C_p = \sum (N_i C_{p,i})_{\text{prod}} - \sum (N_i C_{p,i})_{\text{react}} \quad (1-2)$$

If mean heat capacities \bar{C}_p are known for the reactants and products over the temperature range T_0 to T , it is not necessary to integrate Eq. (1-1). Under these conditions the relationship of ΔH_T and ΔH_{T_0} is

$$\Delta H_T = \Delta H_{T_0} + \sum (N_i \bar{C}_{p,i})_{\text{prod}} (T - T_0) - \sum (N_i \bar{C}_{p,i})_{\text{react}} (T - T_0) \quad (1-3)$$

When reactants and products enter and leave a reactor at different temperatures, it is usually simpler to bypass calculating ΔH_T and evaluate the desired energy quantity directly. This is illustrated in Example 1-1.

The effect of pressure on the heat of reaction for gaseous systems depends on the deviation of the components from ideal-gas behavior. If the reactants and products behave as ideal gases, there is no effect. Even for rather nonideal systems the effect of pressure is generally small. Details of the methods of calculating the effects of temperature and pressure are discussed in standard thermodynamics textbooks.

¹J. W. Andersen, G. H. Beyer, and K. M. Watson, *Natl. Petrol. News, Tech. Sec.* 36 (R476), July 5, 1944; R. H. Ewell, *Ind. Eng. Chem.*, 32, 778 (1940); F. D. Rossini, *Ind. Eng. Chem.*, 29, 1424 (1937); Mott Souders, Jr., C. S. Mathews, and C. O. Hurd, *Ind. Eng. Chem.*, 41, 1037, 1048 (1949); R. C. Reid and T. K. Sherwood "The Properties of Gases and Liquids," 2d ed., chap. 5, McGraw-Hill Book Company, New York, 1966.

²O. A. Hougen and K. M. Watson, "Chemical Process Principles," 2d ed., vol. II, John Wiley & Sons, Inc., New York, 1959.

The application of heat-of-reaction information for calculating energy-transfer rates in reactors is illustrated in the following example.

Example 1-1 Ethylene oxide is produced by direct oxidation with air using a bed of catalyst particles (silver on a suitable carrier). Suppose that the stream enters the flow reactor at 200°C and contains 5 mole % ethylene and 95% air. If the exit temperature does not exceed 260°C, it is possible to convert 50% of the ethylene to the oxide, although 40% is also completely burned to carbon dioxide. How much heat must be removed from the reaction, per mole of ethylene fed, in order not to exceed the limiting temperature? The average molal heat capacity of ethylene may be taken as 18 Btu/(lb mole)(°R) between 25 and 200°C and as 19 Btu/(lb mole)(°R) between 25 and 260°C. Similar values for ethylene oxide are 20 and 21 Btu/(lb mole)(°R). The pressure is essentially atmospheric.

Solution Since heat effects at constant pressure are equal to enthalpy changes, the actual process may be replaced by one that utilizes the available heat-of-reaction data at 25°C (Table 1-1). The steps in this process are

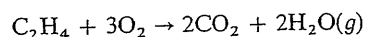
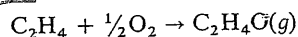
1. Cool the reactants and air from 200 to 25°C.
2. Carry out the reactions at 25°C.
3. Heat the products and the air from 25 to 260°C.

The sum of the enthalpy changes for each step will be the total heat absorbed by the reaction system.

STEP 1 With a basis of 1 mole of ethylene, there will be $\frac{95}{5}(1) = 19$ moles of air fed to the reactor. The mean heat capacity of air from 25°C to 200°C is 7.0. Hence

$$\begin{aligned}\Delta H_1 &= 1(18)(+77 - 392) + 19(7.0)(+77 - 392) = -5,700 - 41,900 \\ &= -47,600 \text{ Btu/lb mole}\end{aligned}$$

STEP 2 The only heat effect is due to the two reactions



Using the heat-of-formation data in Table 1-1, for the first reaction we obtain

$$\begin{aligned}\Delta H_{R_1} &= -12,190 - 12,496 - 0 \\ &= -24,686 \text{ cal/g mole} \quad \text{or} \quad -44,500 \text{ Btu/lb mole}\end{aligned}$$

and for the second

$$\begin{aligned}\Delta H_{R_2} &= 2(-57,798) + 2(-94,052) - 12,496 - 0 \\ &= -316,196 \text{ cal/g mole} \quad \text{or} \quad -569,000 \text{ Btu/lb mole}\end{aligned}$$

Since, per mole of ethylene, there will be 0.5 mole reacting to form ethylene oxide and 0.4 mole to be completely burned,

$$\begin{aligned}\Delta H_{T_0} &= 0.5(-44,500) + 0.4(-569,000) \\ &= -250,000 \text{ Btu/lb mole}\end{aligned}$$

STEP 3 The products will consist of the following quantities:

$$\begin{aligned} \text{Ethylene} &= 1 - 0.5 - 0.4 = 0.1 \text{ mole} \\ \text{Ethylene oxide} &= 0.5 \text{ mole} \\ \text{Water vapor} &= 2(0.4) = 0.8 \text{ mole } (\bar{C}_p = 8.25) \\ \text{Carbon dioxide} &= 2(0.4) = 0.8 \text{ mole } (\bar{C}_p = 9.4) \\ \text{Nitrogen} &= 19(0.79) = 15.0 \text{ moles } (\bar{C}_p = 7.0) \\ \text{Oxygen} &= 19(0.21) - \frac{1}{2}(0.5) - 3(0.4) = 2.6 \text{ moles } (\bar{C}_p = 7.25) \end{aligned}$$

The values shown for \bar{C}_p are mean values between 25 and 260°C:

$$\begin{aligned} \Delta H_3 &= [0.1(19) + 0.5(21) + 0.8(8.25) + 0.8(9.4) + 15(7.0) \\ &\quad + 2.6(7.25)] (500 - 77) \\ &= 150(500 - 77) = 63,500 \text{ Btu/lb mole} \end{aligned}$$

Then the net heat absorbed will be

$$\begin{aligned} Q &= -47,600 - 250,000 + 63,500 \\ &= -234,000 \text{ Btu/lb mole ethylene} \end{aligned}$$

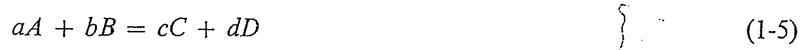
Hence the heat that must be removed is 234,000 Btu/lb mole of ethylene fed to the reactor.

Chemical Equilibrium When a reaction occurs at equilibrium, the temperature and pressure in the system remain constant and the change in free energy is zero. These restraints can be used to develop the following relationship between the *standard* free energy change ΔF° and the equilibrium constant K :

$$\Delta F^\circ = -R_g T \ln K \quad (1-4)$$

The standard free-energy change ΔF° is the difference between the free energies of the products and reactants when each is in a chosen standard state. These standard states are chosen so as to make evaluation of the free energy as simple as possible. For example, for gases the standard state is normally that corresponding to unit fugacity at the temperature of the reaction. If the gas is ideal, this standard state reduces to 1 atm pressure.

The equilibrium constant K is defined in terms of the equilibrium activities a_i of the reactants and products. For a general reaction



the equilibrium constant is

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (1-6)$$

The activities refer to equilibrium conditions in the reaction mixture and

are defined as the ratio of the fugacity in the equilibrium mixture to that in the standard state; that is,

$$a_i = \frac{f_i}{f_i^\circ} \quad (1-7)$$

For gaseous reactions with a standard state of unit fugacity the expression for the equilibrium constant becomes

$$K = \frac{f_C^c f_D^d}{f_A^a f_B^b} \quad (1-8)$$

If, in addition, the gases follow the ideal-gas law, the fugacity is equal to the pressure, and Eq. (1-8) reduces to

$$K = \frac{p_C^c p_D^d}{p_A^a p_B^b} \quad (1-9)$$

Here p (partial pressure) is the total pressure p_t times the mole fraction of the component in the mixture; for example,

$$p_A = p_t y_A \quad (1-10)$$

In many situations the assumption of ideal gases is not justified, and it is necessary to evaluate fugacities. This is the case for such reactions as the ammonia synthesis, where the operating pressure may be as high as 1,500 atm. The fugacity in Eq. (1-8) is that of the component in the equilibrium mixture. However, the fugacity of only the pure component is usually known. To relate the two we must know something about how the fugacity depends on the composition. Normally this information is not available, so that it is necessary to make assumptions about the behavior of the reaction mixture. The simplest and most common assumption is that the mixture behaves as an ideal solution. Then the fugacity at equilibrium, f , is related to the fugacity of the pure component, f' , at the same pressure and temperature by

$$f_i = f' y_i \quad (1-11)$$

Substituting this expression in Eq. (1-8) leads to equations for the equilibrium constant in terms of pure-component fugacities and the composition of the equilibrium mixture,

$$K = \frac{(f'_C)^c (f'_D)^d}{(f'_A)^a (f'_B)^b} K_y \quad (1-12)$$

where

$$K_y = \frac{y_C^c y_D^d}{y_A^a y_B^b} \quad (1-13)$$

In gaseous reactions the quantity K_p is frequently used. This is defined as

$$K_p = \frac{(y_C P_t)^c (y_D P_t)^d}{(y_A P_t)^a (y_B P_t)^b} = K_y P_t^{(c+d)-(a+b)} \quad (1-14)$$

From Eq. (1-9) it is clear that $K = K_p$ for an ideal-gas reaction mixture. For nonideal systems Eq. (1-14) may still be employed to calculate K_p from measured equilibrium compositions (K_y). However, then K_p is not equal to K determined from thermodynamic data, for example, from Eq. (1-4).

Equation (1-12) permits the evaluation of the composition ratio K_y in terms of the equilibrium constant. This is a necessary step toward evaluating the equilibrium conversion from free-energy data. The steps in the process are as follows:

1. Evaluate ΔF° .
2. Determine the equilibrium constant K , using Eq. (1-4).
3. Obtain K_y from Eq. (1-12).
4. Calculate the conversion from K_y .

The first and second steps require thermodynamic data. A brief tabulation of standard free-energy changes ΔF° at 25° is given in Table 1-2. More extensive data have been assembled.¹ Also, estimation procedures have been developed for use when the data are unavailable.²

Usually it is necessary to calculate the effect of temperature on ΔF° in order to obtain an equilibrium constant at reaction conditions. The *van't Hoff equation* expresses this relationship in differential form,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{R_g T^2} \quad (1-15)$$

where ΔH° is the standard-state enthalpy change for the reaction. Equation (1-15) has important implications in reactor design for reversible reactions. It shows that K will decrease with an increase in temperature for an exothermic reaction. Hence provisions must be made for removing the heat of reaction to avoid a thermodynamic limitation (decrease in K) to the potential conversion in exothermic systems. The oxidation of sulfur dioxide is a practical illustration. For endothermic reversible reactions energy must be added to maintain the temperature if a decrease in K is to be avoided. Dehydrogenation of hydrocarbons, such as butanes and butenes, is an example of a situation in which the addition of energy is important. If ΔH°

¹Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Stds. Circ.* 500 1952; Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, *Am. Petrol. Inst. Res. Proj.* 44, Carnegie Institute of Technology, Pittsburgh, 1953.

²R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids," 2d ed., chap. 5, McGraw-Hill Book Company, New York, 1966.

Table 1-2 Standard free energies of formation at 25°C

Substance	Formula	State	ΔF_{f298}°
Normal paraffins			
Methane	CH ₄	<i>g</i>	-12,140
Ethane	C ₂ H ₆	<i>g</i>	-7,860
Propane	C ₃ H ₈	<i>g</i>	-5,614
<i>n</i> -Butane	C ₄ H ₁₀	<i>g</i>	-4,100
<i>n</i> -Pentane	C ₅ H ₁₂	<i>g</i>	-2,000
<i>n</i> -Hexane	C ₆ H ₁₄	<i>g</i>	-70
<i>n</i> -Heptane	C ₇ H ₁₆	<i>g</i>	1,920
<i>n</i> -Octane	C ₈ H ₁₈	<i>g</i>	3,920
Increment per C atom above C ₈		<i>g</i>	2,010
Normal monoolefins (1-alkenes)			
Ethylene	C ₂ H ₄	<i>g</i>	16,282
Propylene	C ₃ H ₆	<i>g</i>	14,990
1-Butene	C ₄ H ₈	<i>g</i>	17,090
1-Pentene	C ₅ H ₁₀	<i>g</i>	18,960
1-Hexene	C ₆ H ₁₂	<i>g</i>	20,940
Increment per C atom above C ₆		<i>g</i>	2,010
Miscellaneous organic compounds			
Acetaldehyde	C ₂ H ₄ O	<i>g</i>	-31,960
Acetic acid	C ₂ H ₄ O ₂	<i>l</i>	-93,800
Acetylene	C ₂ H ₂	<i>g</i>	50,000
Benzene	C ₆ H ₆	<i>g</i>	30,989
Benzene	C ₆ H ₆	<i>l</i>	29,756
1,3-Butadiene	C ₄ H ₆	<i>g</i>	36,010
Cyclohexane	C ₆ H ₁₂	<i>g</i>	7,590
Cyclohexane	C ₆ H ₁₂	<i>l</i>	6,370
Ethanol	C ₂ H ₆ O	<i>g</i>	-40,300
Ethanol	C ₂ H ₆ O	<i>l</i>	-41,770
Ethylbenzene	C ₈ H ₁₀	<i>g</i>	31,208
Ethylene glycol	C ₂ H ₆ O ₂	<i>l</i>	-77,120
Ethylene oxide	C ₂ H ₄ O	<i>g</i>	-2,790
Methanol	CH ₄ O	<i>g</i>	-38,700
Methanol	CH ₄ O	<i>l</i>	-39,750
Methylcyclohexane	C ₇ H ₁₄	<i>g</i>	6,520
Methylcyclohexane	C ₇ H ₁₄	<i>l</i>	4,860
Styrene	C ₈ H ₈	<i>g</i>	51,100
Toluene	C ₇ H ₈	<i>g</i>	29,228
Toluene	C ₇ H ₈	<i>l</i>	27,282
Miscellaneous inorganic compounds			
Ammonia	NH ₃	<i>g</i>	-3,976
Ammonia	NH ₃	<i>aq</i>	-6,370
Calcium carbide	CaC ₂	<i>s</i>	-16,200
Calcium carbonate	CaCO ₃	<i>s</i>	-269,780

Substance	Formula	State	$\Delta F_{f,298}^\circ$
Miscellaneous inorganic compounds (<i>Continued</i>)			
Calcium chloride	CaCl ₂	<i>s</i>	-179,300
Calcium chloride	CaCl ₂	<i>aq</i>	-194,880
Calcium hydroxide	Ca(OH) ₂	<i>s</i>	-214,330
Calcium hydroxide	Ca(OH) ₂	<i>aq</i>	-207,370
Calcium oxide	CaO	<i>s</i>	-144,400
Carbon dioxide	CO ₂	<i>g</i>	-94,260
Carbon monoxide	CO	<i>g</i>	-32,808
Hydrochloric acid	HCl	<i>g</i>	-22,769
Hydrogen sulfide	H ₂ S	<i>g</i>	-7,892
Iron oxide	Fe ₃ O ₄	<i>s</i>	-242,400
Iron oxide	Fe ₂ O ₃	<i>s</i>	-177,100
Iron sulfide	FeS ₂	<i>s</i>	-39,840
Nitric acid	HNO ₃	<i>l</i>	-19,100
Nitric acid	HNO ₃	<i>aq</i>	-26,410
Nitrogen oxides	NO	<i>g</i>	20,719
	NO ₂	<i>g</i>	12,390
	N ₂ O	<i>g</i>	24,760
	N ₂ O ₄	<i>g</i>	23,491
Sodium carbonate	Na ₂ CO ₃	<i>s</i>	-250,400
Sodium chloride	NaCl	<i>s</i>	-91,785
Sodium chloride	NaCl	<i>aq</i>	-93,939
Sodium hydroxide	NaOH	<i>s</i>	-90,600
Sodium hydroxide	NaOH	<i>aq</i>	-100,184
Sulfur dioxide	SO ₂	<i>g</i>	-71,790
Sulfur trioxide	SO ₃	<i>g</i>	-88,520
Sulfuric acid	H ₂ SO ₄	<i>aq</i>	-177,340
Water	H ₂ O	<i>g</i>	-54,635
Water	H ₂ O	<i>l</i>	-56,690

NOTES: The standard free energy of formation $\Delta F_{f,298}^\circ$ is the change in free energy when the listed compound is formed from its elements with each substance in its standard state at 298°K (25°C). Standard states are:

1. Gases (*g*), the pure gas at unit fugacity and 25°C
2. Liquids (*l*) and solids (*s*), the pure substance at atmospheric pressure and 25°C
3. Solutes in aqueous solution (*aq*), the hypothetical 1-molal solution of the solute in water at atmospheric pressure and 25°C

The units of ΔF° are calories per gram mole of the listed substance.

SOURCE: Selected mainly from F. D. Rossini et al., Selected Values of Properties of Hydrocarbons and Related Compounds, *Am. Petrol. Inst. Res. Proj. 44*, Carnegie Institute of Technology, Pittsburgh, 1953, and loose-leaf supplements (by permission); F. D. Rossini et al., in D. D. Wagman (ed.), Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Stds. Circ. 500*, 1952, and loose-leaf supplements.

is approximately independent of temperature, the integrated form of Eq. (1-15) is

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{-\Delta H^\circ}{R_g} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1-16)$$

If ΔH° is not constant, but can be expressed by Eq. (1-1), the integrated form is

$$\ln K_T = -\frac{\Delta H_0}{R_g T} + \frac{\Delta a}{R_g} \ln T + \frac{\Delta b}{2R_g} T + \frac{\Delta c}{6R_g} T^2 + C \quad (1-17)$$

where ΔH_0 , C , and Δa , Δb , and Δc are constants and Δa , Δb , and Δc arise from the expression

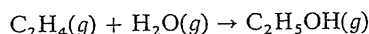
$$\Delta C_p = \Delta a + \Delta b T + \Delta c T^2 \quad (1-18)$$

K can be determined from Eqs. (1-17) and (1-18) for a gaseous reaction at any temperature, provided the constants C and ΔH_0 can be evaluated. Experimental data for K at two temperatures is sufficient for this evaluation. Alternately, ΔH_0 can be found from the known heat of reaction at one temperature with Eq. (1-1). In this case only one experimental value of the equilibrium constant is needed in order to determine the constant C . Of course, in both methods it is necessary to have heat-capacity data for reactants and products in order to evaluate the coefficients Δa , Δb , and Δc .

Application of the foregoing concepts in evaluating the equilibrium conversion from free-energy data is illustrated by the following examples.

Example 1-2 The following equilibrium data have been reported for the vapor-phase hydration of ethylene to ethanol:¹ at 145°C $K = 6.8 \times 10^{-2}$ and at 320°C $K = 1.9 \times 10^{-3}$. From these data develop general expressions for the equilibrium constant as a function of temperature.

Solution From the two values of K the constants ΔH_0 and C in Eq. (1-17) may be determined. First the values of Δa , Δb , and Δc must be obtained from heat-capacity data. For the reaction



these are

$$\Delta = C_2\text{H}_5\text{OH} - \text{C}_2\text{H}_4 - \text{H}_2\text{O}$$

$$\Delta a = 6.990 - 2.830 - 7.256 = -3.096$$

$$\Delta b = 0.039741 - 0.028601 - 0.002298 = 0.008842$$

$$\Delta c = (-11.926 + 8.726 - 0.283) \times 10^{-6} = -3.483 \times 10^{-6}$$

¹H. M. Stanley et al., *J. Soc. Chem. Ind.*, 53, 205 (1934); R. H. Bliss and B. F. Dodge, *Ind. Eng. Chem.*, 29, 19 (1937).

Substituting these values in Eq. (1-17), we have, at 145°C,

$$R_g \ln (6.8 \times 10^{-2}) = -\frac{\Delta H_0}{418} - 3.096 \ln 418 + \frac{0.00884}{2} (418) - \frac{3.483 \times 10^{-6}}{6} (418)^2 + CR_g$$

or

$$\frac{\Delta H_0}{418} - CR_g = -R_g \ln (6.8 \times 10^{-2}) - 3.096 \ln 418 + 0.00442(418) - (0.580 \times 10^{-6})(418)^2 = -11.59 \quad (\text{A})$$

and at 320°C

$$\frac{\Delta H_0}{593} - CR_g = -R_g \ln (1.9 \times 10^{-3}) - 3.096 \ln 593 + 0.00442(593) - (0.580 \times 10^{-6})(593)^2 = -4.91 \quad (\text{B})$$

Equations (A) and (B) may be solved simultaneously for ΔH_0 and C . The results are

$$\Delta H_0 = -9460 \text{ cal}$$

$$C = -5.56$$

Then the general expression for K as a function of temperature is

$$\ln K = \frac{9,460}{R_g T} - \frac{3.096}{R_g} \ln T + \frac{0.00442}{R_g} T - \frac{0.580 \times 10^{-6}}{R_g} T^2 - 5.56$$

or

$$\ln K = \frac{4,760}{T} - 1.558 \ln T + 0.00222T - 0.29 \times 10^{-6} T^2 - 5.56$$

Example 1-3 Estimate the maximum conversion of ethylene to alcohol by vapor-phase hydration at 250°C and 500 psia. Use the equilibrium data of Example 1-2 and assume an initial steam-ethylene ratio of 5.

Solution The equilibrium constant at 250°C can be evaluated from the equation for K developed in Example 1-2:

$$\begin{aligned} \ln K &= \frac{4,760}{523} - 1.558 \ln 523 + 0.00222(523) - 0.29 \times 10^{-6}(523)^2 - 5.56 \\ &= -5.13 \end{aligned}$$

$$K = 5.9 \times 10^{-3}$$

It is necessary to assume that the gas mixture is an ideal solution. Then Eq. (1-12) is applicable, and

$$5.9 \times 10^{-3} = K_y \frac{f'_A}{f'_E f'_W} \quad (\text{A})$$

The fugacities of the pure components can be determined from generalized correlations¹ and are evaluated at the temperature and pressure of the equilibrium mixture:

$$\frac{f'_A}{P_t} = 0.84 \quad \text{for ethanol}$$

$$\frac{f'_E}{P_t} = 0.98 \quad \text{for ethylene}$$

$$\frac{f'_W}{P_t} = 0.91 \quad \text{for water}$$

Substituting these data in Eq. (A), we have

$$K_y = \frac{y_A}{y_E y_W} = 5.9 \times 10^{-3} \frac{0.98(0.91)}{0.84} \frac{500}{14.7} = 0.21 \quad (\text{B})$$

If the initial steam-ethylene ratio is 5 and a basis of 1 mole of ethylene is chosen, a material balance gives the following results for equilibrium conditions:

$$\text{Ethanol} = z$$

$$\text{Ethylene} = 1 - z$$

$$\text{Water} = 5 - z$$

$$\text{Total moles} = 6 - z$$

Then

$$y_A = \frac{z}{6 - z}$$

$$y_E = \frac{1 - z}{6 - z}$$

$$y_W = \frac{5 - z}{6 - z}$$

Substituting in Eq. (B), we have

$$0.21 = \frac{z(6 - z)}{(1 - z)(5 - z)}$$

$$z^2 - 6.0z + 0.868 = 0$$

$$z = 3.0 \pm 2.85 = 5.85 \quad \text{or} \quad 0.15$$

The first solution is greater than unity and is impossible. Therefore $z = 0.15$, indicating that 15% of the ethylene could be converted to ethanol, provided that equilibrium were achieved.

¹For example from J. M. Smith and H. C. Van Ness, "Introduction to Chemical Engineering Thermodynamics," fig. 12-1, McGraw-Hill Book Company, New York, 1959.

In this reaction increasing the temperature decreases K and the conversion. Increasing the pressure increases the conversion. From an equilibrium standpoint the operating pressure should be as high as possible (limited by condensation) and the temperature as low as possible. A catalyst is required to obtain an appreciable rate, but all the catalysts that are presently available require a temperature of at least 150°C for a reasonably fast rate. Even at this temperature the catalysts which have been developed will give no more than a fraction of the equilibrium conversion. In this instance both equilibrium and reaction rate limit the commercial feasibility of the reaction process.

1-6 Classification of Reactors

Chemical reactors may have a great variety of sizes, shapes, and operating conditions. One of the most common is the small flask or beaker used in the chemical laboratory for liquid-phase reactions. At the other extreme in size are the large cylindrical vessels used in the petroleum industry (for example, in the cracking of hydrocarbons), which may be up to 40 ft in diameter. In the laboratory beaker a charge of reactants is added, brought to reaction temperature, held at this condition for a predetermined time, and then the product is removed. This *batch reactor* is characterized by the variation in extent of reaction and properties of the reaction mixture with time. The hydrocarbon-cracking reactor operates continuously with a steady flow of reactants in and products out. This is the continuous-flow type, in which the extent of reaction may vary with position in the reactor but not with time. Hence one classification of reactors is according to method of operation.

Another classification is according to shape. If the laboratory vessel is equipped with an efficient stirrer, the composition and temperature of the reaction mass will tend to be the same in all parts of the reactor. A vessel in which the properties are uniform is called a *stirred-tank* (or well-mixed) *reactor*. If there is no mixing in the direction of flow in the cylindrical vessel for hydrocarbon processing, another ideal type is realized: the *ideal tubular-flow*, or *plug-flow reactor*. Here the reaction mass consists of elements of fluid that are independent of each other, each one having a different composition, temperature, etc. This classification is of basic significance in design, because simplified treatments of the physical processes of mass and energy transfer are applicable for each ideal reactor. We noted in Sec. 1-1 that evaluation of the importance of such processes is at the heart of the design problem.

The two classifications, batch or continuous and tank or tube, are independent. Thus the laboratory beaker can be made into a continuous-flow type, and often is, by adding tubes for continuous addition of reactants

and withdrawal of products. Proper reactor shape and stirring arrangement will ensure ideal stirred-tank behavior.

A third classification is based on the number of phases in the reaction mixture. The significance of this classification is also due to the influence of physical processes. A common type of *heterogeneous* reaction is illustrated by the oxidation of sulfur dioxide with a vanadium pentoxide catalyst (solid phase). The overall production of sulfur trioxide can depend on the mass-transfer process in transporting sulfur dioxide from the gas phase to the surface of the solid catalyst. This physical process results from the fact that the reaction system is heterogeneous; it would not exist if the reaction were a single-phase, or *homogeneous*, system. Note also that the catalytic nature of the reaction is not responsible for the diffusional resistance. The same type of physical process is involved in smelting reactions, such as the gas-solid noncatalytic reaction between oxygen and zinc sulfide to form zinc oxide.

In summary, the three classifications of reactors of importance in design are (1) batch or continuous, (2) tank or tubular, and (3) homogeneous or heterogeneous. We shall consider them in detail beginning with Chap. 4. The classification by shape offers numerous possibilities. A few modifications of the tank and tube types are shown in Fig. 1-3. The tubular type can be made to approach the tank type as far as mixing is concerned by recirculating part of the product (Fig. 1-3a). The tubular-flow reactor can be arranged to give an increasing flow area by employing a radial-flow arrangement (Fig. 1-3c). This could be useful for a gaseous reaction accompanied by a large increase in number of moles (volume).

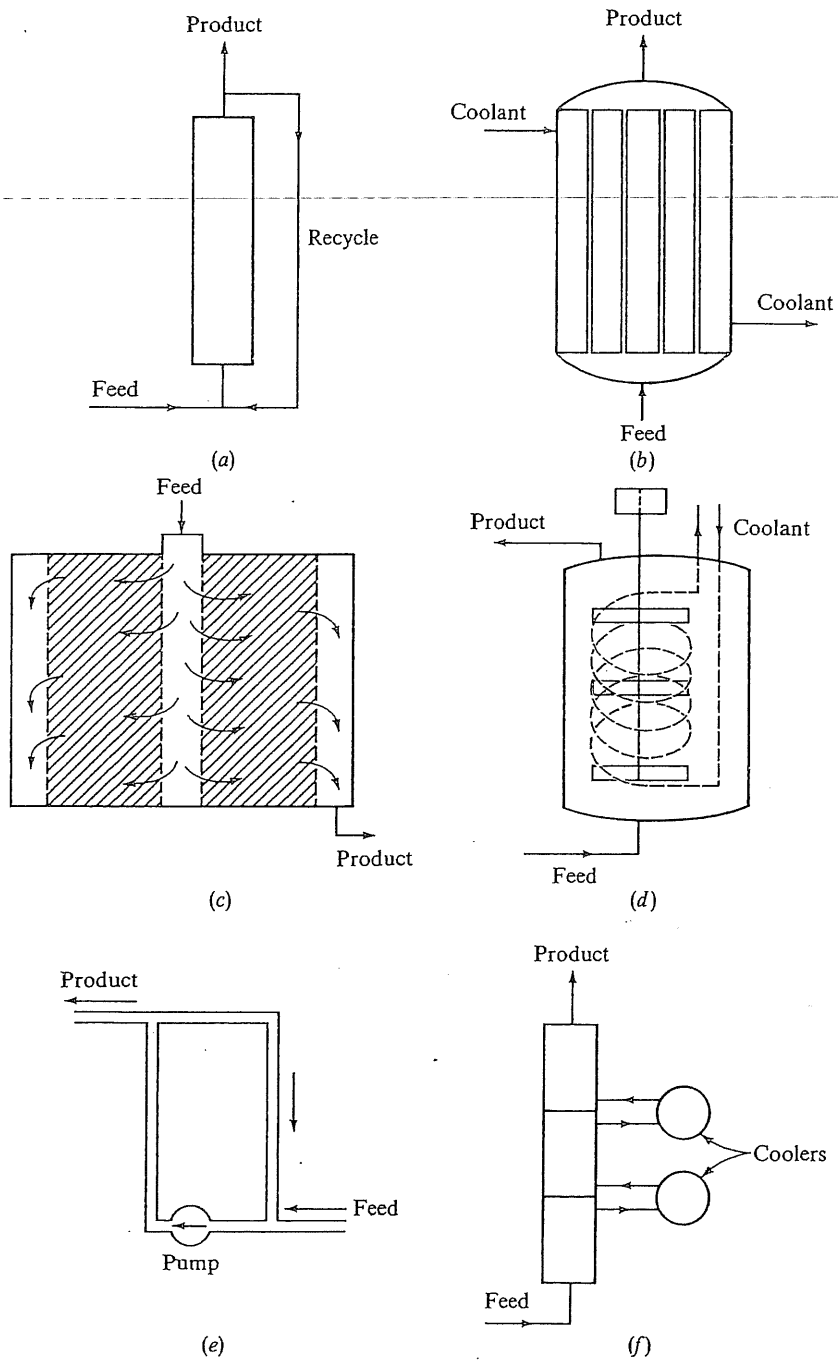
Equipment for heterogeneous reactions is particularly flexible, since each phase can be processed more or less independently. In the fluidized-bed reactor (Fig. 1-4) the reactants flow continuously through and out of the reactor, but the solid-catalyst phase is withdrawn, regenerated, and returned. In the lime kiln (an example of a gas-solid noncatalytic reactor) the two phases pass continuously and countercurrently through the reactor. In heterogeneous liquid-solid polymerization systems the slurry of catalyst and reaction mixture flow together through the reactors. Walas,¹ Brotz,² and particularly van Krevelen³ have summarized the various types of

¹S. M. Walas, "Reaction Kinetics for Chemical Engineers," McGraw-Hill Book Company, New York, 1959.

²W. Brotz, "Fundamentals of Chemical Reaction Engineering," translated by D. A. Diener and J. A. Weaver, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965.

³D. W. van Krevelen, *Chem. Eng. Sci.*, 8, 5 (1958).

Fig. 1-3 Typical reactors (a) tubular-flow recycle reactor, (b) multitube-flow reactor, (c) radial-flow catalytic reactor, (d) stirred-tank reactor with internal cooling, (e) loop reactor, (f) reactor with intercoolers (opposite)



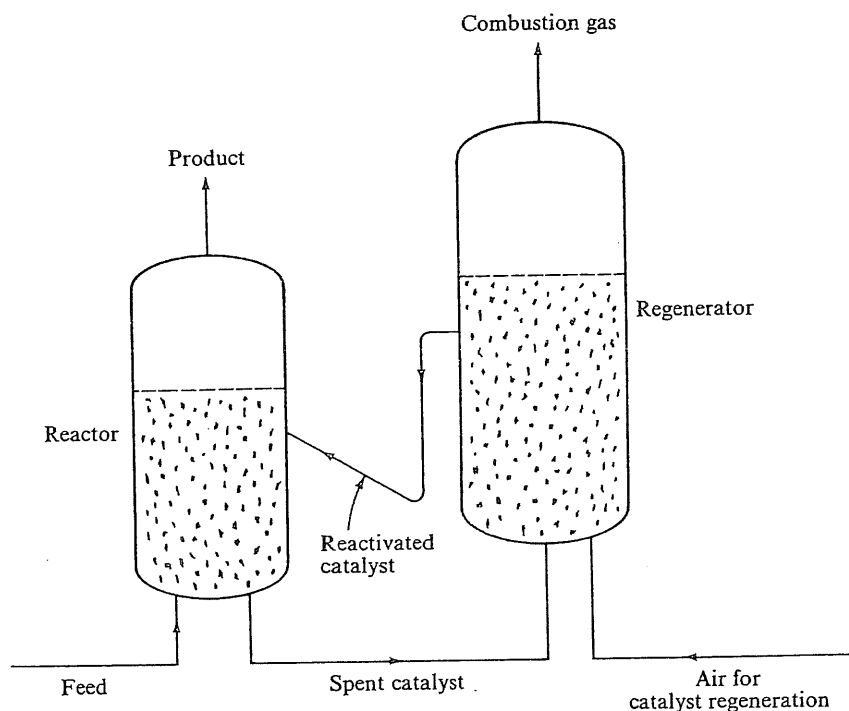


Fig. 1-4 Fluidized-bed reactor-regenerator system

heterogeneous reactors used industrially. Despite the multitude of possibilities, the performance of each reactor can be described adequately as a combination or adaptation of the three basic types.

There are some general relations between the physical nature of the reaction mixture and the type of reactor used in practice. Thus homogeneous gas-phase reactions are normally carried out in continuous-tubular-flow reactors rather than the tank type, either batch or flow. For liquid-phase and liquid-solid-phase heterogeneous reactions, both tank and tubular-flow reactors are employed. When a tank-type reactor is indicated but the operating pressure is so high that large-diameter vessels are too expensive, the same well-mixed condition can be obtained by circulating the reaction mixture in a loop (Fig. 1-3e). Batch-operated tank reactors are often used for small-scale production and when flexible operating conditions (temperature and pressure) are required. Such systems frequently involve costly reactants and products, as in the pharmaceutical industry.

Heat-transfer requirements can affect both the form of a reactor and its type. For example, the removal of large amounts of energy in a tank-

type reactor can be achieved by introducing cooling coils to supply the required heat-transfer area. Similarly, in a tubular-flow reactor the heat-transfer rate can be increased by increasing the number and decreasing the diameter of the tubes used in parallel (Fig. 1-3*b*) or by using intercoolers (Fig. 1-3*f*). When it is necessary to approach isothermal conditions or when the heats of reaction are large, a fluidized-bed type is often used.

The chapters that follow deal with the interpretation of laboratory rate data for the design of large-scale reactors. We have seen that two aspects of chemistry, chemical thermodynamics (Sec. 1-5) and chemical kinetics, are necessary to provide the proper foundation for achieving this objective. Kinetics will be discussed in Chap. 2. We have also seen that an understanding of physical processes, particularly mass and energy transfer, is required. The interaction of chemical kinetics and physical processes depends on the type of reactor (recall the illustration for para-hydrogen conversion). Hence their study cannot be undertaken independently of the reactor-design problem. In this chapter the major classifications of reactors have been presented. Some concepts are common to all classifications, and these are discussed in Chap. 3. The remainder of the book is devoted to the design of different types of reactors. Design for homogeneous reactions is considered in Chaps. 4 to 6, and Heterogeneous systems are discussed in Chaps. 7 to 14. Since many heterogeneous reactions involve catalysts, the nature and kinetics of catalytic reactions are treated separately in Chaps. 8 and 9. In this chapter physical processes in the design of heterogeneous reactors has been emphasized; quantitative analysis of these processes is given in Chaps. 10 and 11.

Bibliography

There are several books which have as their objective the application of kinetics to chemical reactor design. The subject has been treated differently in each of these texts, and each is worthwhile for supplementary reading. A partial list is as follows:

1. Rutherford Aris, "Elementary Chemical Reactor Analysis," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1969. A rather broad, analytical book in which theory of the general case is presented first and then followed with applications.
2. K. G. Denbigh, "Chemical Reactor Theory," Cambridge University Press, Cambridge, 1965. This small, very clearly written book provides an excellent treatment of the important problems in chemical reactor design.
3. O. A. Hougen and K. M. Watson, "Chemical Process Principles," part 3, Kinetics and Catalysis, John Wiley & Sons, Inc., New York, 1947. The principles of flow

- reactors were first presented in this book. Design calculations are given for several industrially important reactions.
4. H. Kramers and K. R. Westerterp, "Chemical Reactor Design and Operation," Academic Press, Inc., New York, 1963. A concise treatment of a few selected subjects of reactor design, including optimization and residence-time distributions.
 5. Octave Levenspiel, "Chemical Reaction Engineering," John Wiley & Sons, Inc., New York, 1962. A complete text for undergraduate students. The emphasis is rather more on homogeneous and noncatalytic reactors than on catalytic ones. Effects of residence-time distribution on reactor performance are treated in detail.
 6. E. E. Petersen, "Chemical Reaction Analysis," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965. A more advanced text emphasizing fluid-solid catalytic reactions and reactor design.

Problems

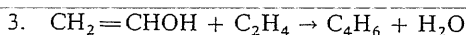
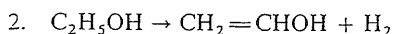
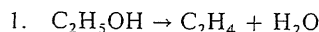
- 1-1. Water vapor is 1.85 mole % dissociated at 2000°C and 1 atm total pressure, at equilibrium. Calculate the equilibrium dissociation at 25°C and 1 atm.
- 1-2. Consider a reactor in which two gas-phase reactions occur:
 1. $A + B \rightarrow C + D$
 2. $A + C \rightarrow 2E$

At the reaction temperature, $K_{p_1} = 2.667$ and $K_{p_2} = 3.200$. The total pressure is 10 atm, and the feed to the reactor has a composition of 2 moles of A and 1 mole of B . Calculate the composition of the reactor effluent if equilibrium is attained with respect to both reactions.
- 1-3. (a) Assuming that the only reaction involved is the dehydrogenation to vinyl alcohol, estimate the equilibrium constant and equilibrium yield of vinyl alcohol from ethanol at 400°F and 1 atm pressure. (b) Determine the composition of the gases at equilibrium obtained by dehydrogenating ethanol at 400°F and 1 atm pressure, this time considering the formation of both vinyl alcohol and acetaldehyde. The group-contribution method may be helpful in estimating thermodynamic properties. (See reference to O. A. Hougen and K. M. Watson p. 1004, Part II, Second Edition).
- 1-4. One mechanism that has been proposed for the conversion of ethyl alcohol to butadiene in the vapor phase consists of three steps: (a) dehydration of the ethyl alcohol; (b) dehydrogenation of the ethyl alcohol; (c) condensation of the ethylene and acetaldehyde in (a) and (b) to give butadiene, C_4H_6 . At 400°C the following information is available for the three steps:
 - (a) $\Delta F^\circ = -10,850$ cal/g mole
 - (b) $\Delta F^\circ = -3610$ cal/g mole
 - (c) $\Delta F^\circ = -1380$ cal/g mole

Determine the conversion of alcohol to butadiene at 400°C and 1 atm total

pressure. For uniformity let α be the extent of reaction 1 and β the extent of reaction 2, and let γ be the moles of butadiene at equilibrium.

- 1-5. Another mechanism which has been proposed for the overall reaction in Prob. 1-4 is



Is there any simple relationship between (a) the equilibrium constants for these reactions and the reactions in Prob. 1-4 and (b) the conversion to butadiene for these reactions and the reactions in Prob. 1-4.

- 1-6. Calculate the dissociation pressure of $\text{Ag}_2\text{O}(s)$ at 200°C . Use the following data:

$$\left. \begin{array}{l} \Delta H^\circ = 6950 \text{ cal/g mole} \\ \Delta F^\circ = 2230 \text{ cal/g mole} \end{array} \right\} \text{ at } 25^\circ\text{C}$$

$$C_p = \begin{array}{ll} 5.60 + 1.5 \times 10^{-3} T & \text{for Ag}(s) \\ 6.50 + 1.0 \times 10^{-3} T & \text{for O}_2(g) \end{array}$$

where T is in degrees Kelvin.

- 1-7. Assuming that the value of K_p for the methanol-synthesis reaction is 9.28×10^{-3} at 1 atm pressure and 300°C , what are the numerical values of the following quantities at this temperature?

- K at $p_t = 1$ atm
- K_p at $p_t = 10$ atm
- K_p at $p_t = 50$ atm
- K at 10 and 50 atm total pressure
- K_y at 1, 10, and 50 atm total pressure

- 1-8. Newton and Dodge¹ and von Wettberg and Dodge² measured the composition of equilibrium mixtures of CO , H_2 , and CH_3OH in the methanol synthesis. Compute the value of K and ΔF° at 309°C from the following data taken from their work:

$$t = 309^\circ\text{C}$$

$$p_t = 170 \text{ atm}$$

The equilibrium gas analysis, in mole %, is

$$\text{Hydrogen} = 60.9$$

$$\text{Carbon monoxide} = 13.5$$

$$\text{Methanol} = 21.3$$

¹J. Am. Chem. Soc., 56, 1287 (1934).

²Ind. Eng. Chem., 22, 1040 (1930).

Inerts = 4.3
Total = 100.0

1-9. The complete results referred to in Prob. 1-8 are as follows:

$1,000/T, ^\circ\text{K}^{-1}$	1.66	1.73	1.72	1.75	1.82	1.81	1.82	1.82
$\log K$	-4.15	-3.75	-3.65	-3.30	-3.10	-3.20	-3.00	-2.90
	1.83	1.88	1.91	1.91	1.92	2.05	2.05	2.05
	-2.95	-2.60	-2.70	-3.00	-2.30	-2.30	-2.15	-2.35

From this information determine the best relationship between K and T in the form

$$\ln K = A \frac{1}{T} + B$$

1-10. The determination of K in Prob. 1-8 was based on direct measurement of equilibrium compositions. Use the calorimetric data below and the third law to prepare a plot of $\log K$ vs $1/T$ for the methanol synthesis. Include a temperature range of 298 to 800°K. Compare the graph with the result obtained in Prob. 1-9.

The entropy of CO gas at 298.16°K in the ideal-gas state at 1 atm is 47.30 cal/(g mole)(°K). A similar value for hydrogen is 31.21. The heat of vaporization for methanol at 298.16°K is 8943.7 cal/g mole, and the vapor pressure at 298.16°K is 0.1632 atm. Heat of formation of CH_3OH in the ideal-gas state at 1 atm is -48,490 cal/g mole. Low-temperature specific-heat and heat-of-transition data for methanol are as follows:

$T, ^\circ\text{K}$	18.80	21.55	24.43	27.25	30.72	34.33	37.64	40.87
$C_p, \text{ cal/}$ $(\text{g mole})(^\circ\text{C})$	1.109	1.512	1.959	2.292	2.829	3.437	3.962	4.427
	43.93	48.07	56.03	59.53	63.29	69.95	73.95	77.61
	4.840	5.404	6.425	6.845	7.252	8.001	8.392	8.735
	81.48	85.52	89.29	93.18	97.22	111.14	111.82	117.97
	9.001	9.295	9.693	9.939	10.23	11.23	11.48	11.64
	118.79	121.44	125.07	129.38	133.71	147.86	152.29	153.98
	11.64	11.74	12.18	12.28	12.64	12.97	13.69	14.12

164.14	166.23	167.75	181.09	185.10	189.06	196.77	210.34
11.29	11.63	11.68	16.60	16.67	16.77	16.78	16.97
235.84	256.34	273.58	285.15	292.01			
17.41	17.70	18.30	18.70	19.11			

Methanol crystals undergo a phase transition at 157.4°K for which $\Delta H = 154.3$ cal/g mole. The melting point is 175.22°K, and the heat of fusion is 757.0 cal/g mole. Specific-heat data at temperatures above 298.16°K are as follows:

$T, ^\circ\text{K}$	298.16	300	400	500	600	700	800
$C_p, \text{CH}_3\text{OH}, \text{cal}/(\text{g mole})(^\circ\text{C})$	10.8	10.8	12.7	14.5	16.3	17.8	19.2
$T, ^\circ\text{C}$	25	100	200	300	400	500	600
$(c_p)_{\text{CO}}, \text{cal}/(\text{g})(^\circ\text{C})$	0.249	0.250	0.253	0.258	0.264	0.271	0.276
$(c_p)_{\text{H}_2}, \text{cal}/(\text{g})(^\circ\text{C})$	3.42	3.45	3.47	3.47	3.48	3.50	3.53