CH 204: Chemical Reaction Engineering - lecture notes

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Introduction

Levenspiel (2004, p. iii) has given a concise and apt description of chemical reaction engineering (CRE):

> Chemical reaction engineering is that engineering activity concerned with the exploitation of *chemical reactions* on a *commercial* scale. Its goal is the successful *design* and *operation* of chemical reactors, and probably more than any other activity, it sets chemical engineering apart as a distinct branch of the engineering profession.

The ingredients of CRE are (i) thermodynamics, (ii) kinetics, (iii) tranport processes, (iv) types of reactors, (v) mode of operation and contacting, (vi) modelling and optimization, and (vii) control. These topics are briefly discussed below.

1.1 Thermodynamics

1.1.1 Feasibility of the reaction

The standard free energy of formation ΔG_0 of gaseous NO at a temperature $T = 298$ K and a reference pressure $p_0 = 1$ atm is 86.6 kJ/mol. Consider a closed system that initially contains a mixture of N_2 and O_2, and is maintained at a constant temperature T and a pressure $p = p_0$. Consider the reaction

$$\frac{1}{2}\mathrm{N_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \rightleftharpoons \mathrm{NO(g)} \tag{1.1}$$

Here the notation "(g)" implies that the species is present in the gas phase. Similarly, "(l)" and "(s)" will be used to denote species present in the liquid and solid phases. respectively. Some NO will be formed by (1.1), but the *equilibrium* mole fraction of NO ($y_{\mathrm{NO},e}$) is $\ll 1$ as $\Delta G_0/(RT) \gg 1$. Here R

is the gas constant, and $y_{\mathrm{NO},e}$ is the mole fraction attained at long times. Hence we say that the reaction is not feasible under these conditions. The conversion increases as T increases, but is less than 1 % even at $T = 1780$ K and $p = 1$ atm. Hence alternative reactions, such as the oxidation of NH_3 must be used to produce NO (Chatterjee and Joshi, 2008).

1.1.2 The heat of reaction

The *sign* of the heat of reaction ΔH determines whether the reactor should be heated or cooled. The former applies for *endothermic* reactions ($\Delta H > 0$), and the latter for *exothermic* reactions ($\Delta H < 0$). The *magnitude* of ΔH determines the amount of heating or cooling required.

1.1.3 Allowance for thermodynamic non-idealities

For gaseous reactions at high pressure or low temperature, the equilibrium constant K_p, which is based on partial pressures, must be replaced by the equilibrium constant K_f, which is based on fugacities (Denbigh, 1971, p. 152, see also section 2.8). For example, consider the *ammonia synthesis* reaction

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)} \tag{1.2}$$

At $T = 450°\mathrm{C}$, the value of K_p is 6.64 $\times 10^{-3}$ at $p = 10$ atm and 8.84 $\times 10^{-3}$ at $p = 300$ atm (Denbigh, 1971, p. 152). Thus K_p varies with the pressure, whereas the value of K_f is approximately constant in this pressure range - it is 6.5 $\times 10^{-3}$ at $p = 10$ atm and 6.6 $\times 10^{-3}$ at $p = 300$ atm. The slight variation of K_f is caused by the use of approximate expressions for the fugacities, based on the Lewis and Randall rule. Given the value of ΔG_0, we can calculate K_f, and using the thermodynamic relations between fugacities and partial pressures, the equilibrium composition can be calculated.

Similarly, for a liquid phase reaction involving the synthesis of methyl tert-amyl ether (an additive for high octane gasoline) from methanol and 2-methyl-2-butene, the calculated activity coefficient for methanol is in the range 6.4-7.7 at $T = 298$ K (Heintz et al., 2007).

1.2 Reactions and kinetics

1.2.1 Classification of reactions

Reactions may be classified by (a) the number of phases involved, (b) the presence or absence of a catalyst, and (c) the nature of the overall reaction.

If all the reactants and products, and catalysts, if any, are in a *single* phase, the reaction is said to be *homogeneous.* An example is provided by the *thermal cracking* of ethane to ethylene (Froment and Bischoff, 1990, p. 29)

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \tag{1.3}$$

On the other hand, if more than one phase is involved, the reaction is said to be *heterogeneous.* An example is provided by the chemical vapour deposition (CVD) of Si on a substrate (Fogler, 1999, p. 675)

$$\begin{array}{lcl} SiH_4(g) & \rightarrow & Si(s) + 2\,H_2(g) \\ \text{(silane)} & & \end{array} \tag{1.4}$$

Equation (1.3) represents a *non-catalytic* reaction, whereas ammonia synthesis involves a solid catalyst. In some cases, a homogeneous catalyst may be involved. For example, an enzyme called *glucose isomerase* catalyzes the isomerization of glucose to fructose in the liquid phase (Fig. 1.1).

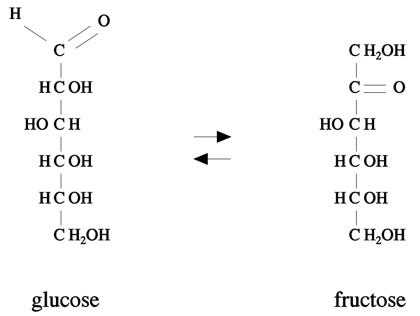

Fig. 1.1. Isomerization of glucose to fructose. Adapted from Schmidt (2005, p. 24).

Schmidt (2005, p. 24) notes that this is the largest bioprocess in the chemical industry. As fructose is five times sweeter than glucose, the process is used to make high-fructose corn syrup for the soft drink industries.

The overall reaction, *as written*, may represent either an *elementary* reaction or a *non-elementary* reaction. An example of the former is given by the gas-phase reaction (Laidler, 2007, p. 138)

$$NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g) \tag{1.5}$$

Here NO is formed by the collision between molecules of NO_2 and CO, and the rate expression conforms to the stoichiometry shown. On the other hand, (1.4) represents a non-elementary reaction, as it actually proceeds by the sequence of reactions shown below (Fogler, 1999, p. 666).

$$\begin{aligned} SiH_4(g) &\rightleftharpoons SiH_2(g) + H_2(g) \\ SiH_2(g) + * &\rightarrow SiH_2 * \\ SiH_2 * &\rightarrow Si(s) + H_2(g) \end{aligned} \tag{1.6}$$

where * represents an active site on the substrate.

1.2.2 The rate expression

The *rate expression* provides information about the rate at which a reactant is consumed. The rate is usually expressed per unit volume of the fluid for fluid-phase reactions, and per unit area (or unit mass) of the catalyst for reactions involving solid catalysts. For example, the rate of formation of Si by the mechanism (1.6) is given by

$$\dot{r}_{Si} = \frac{k\, p_{SiH_4}}{p_{H_2} + K\, p_{SiH_4}} \tag{1.7}$$

where p_{SiH_4} and p_{H_2} are the partial pressures of SiH_4 and H_2, respectively.

Equation (1.7) can be derived from (1.6) by assuming that the reactions follow *mass action* kinetics and invoking some other assumptions.

1.2.3 Alternative catalysts or alternative routes

The conventional process for the manufacture of 5-cyanovaleramide (an intermediate for a herbicide) by the hydrolysis of adiponitrile (Fig. 1.2) used MgO as a catalyst (Pereira, 1999). The catalyst was difficult to recover and reactivate, and the conversion had to be limited to 20 % to avoid a low selectivity. An alternative process based on a supported enzyme catalyst gave a high conversion and a high selectivity.

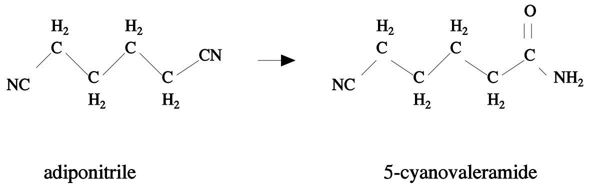

Fig. 1.2. Conversion of adiponitrile to 5-cyanovaleramide.

1.3 Transport processes

1.3.1 Balance equations

For fluid-phase reactions, *continuum* equations are usually used. If the reactions involve two phases that are stratified, as in the case of a gas-liquid reaction in a falling-film reactor, separate equations can be written for each of the phases. If one phase is dispersed in the other, as in the case of stirred liquid-liquid dispersions or fluidized beds, we can either write separate equations for each phase, or use some form of explicit or implicit averaging to write continuum equations for each phase (see. for example, Jackson, 2000, Yu et al., 2007).

1.3.2 Constitutive equations

For a fluid phase consisting of simple fluids such as air or water, the Navier-Stokes equations are commonly used to describe momentum transfer, with Fourier's law for heat conduction. Diffusion is described either by Fick's law for binary mixtures, or by the Maxwell-Stefan equations for multicomponent mixtures. For a *stationary* solid phase such as a bed of catalyst pellets, the momentum balance is not required. However, Fourier's law and Fick's law have to be modified by replacing the thermal conductivity and diffusivity by the "effective" thermal conductivity and "effective" diffusivity, respectively.

For dispersed multiphase systems, constitutive equations are more complicated, and not as firmly established as for single-phase systems.

1.4 Types of reactors

1.4.1 Ideal reactors

The adjective ideal refers to the state of *mixing* in the reactor. It is assumed to be perfect in the case of ideal *batch*, *semi-batch*, and *continuous stirred tank* reactors. The *plug flow* reactor corresponds to the assumption of *perfect* mixing in the radial direction, *no* mixing in the axial direction, and a *flat* axial velocity profile. As discussed in Levenspiel (2004, pp. 283-287, 321-334) and Fogler (1999, pp. 873-876, 893-904) a sequence of ideal reactors can sometimes be used to model nonideal reactors.

1.4.2 Actual reactors

In addition to the conventional stirred vessels, "empty" tubular reactors, and packed beds, there are many other types of reactors such as *fluidized beds* (Lee and Li, 2009), *trickle beds* (Wu et al., 2009), *fluidized catalytic crackers* (Yang et al., 2009), *bubble columns* (Tokumura et al., 2009), *membrane reactors* (Rahimpour and Ghader, 2004), *microchannel reactors* (Wang et al., 2009), and *multifunctional reactors* (Fan et al., 2009; Agar, 1999). The references in brackets represent recent articles discussing such reactors.

1.5 Mode of operation and contacting

Reactors can be operated either in *batch*, *semi-batch* or *continuous* modes. The first two modes cause the concentrations of the species to vary with time, whereas the latter can be operated in either a *steady* or *unsteady* manner. Usually, startup, shutdown, and disturbances in feed flow rate, etc. lead to unsteady operation. For some systems, it may be advantageous to deliberately operate in an unsteady manner to achieve higher selectivity or conversion. For example, Sotowa et al. (2008) examined the effect of forced temperature cycling of a catalyst layer on propylene (C_3H_6) oxidation. They found the forced operation led to a higher time-averaged conversion than steady state operation, for the same rate of consumption of energy. The *bombardier beetle* provides an example of a natural system that relies on *forced periodic operation* (Aneshansley et al., 1969).

For multiphase reactors, several modes of contacting, such as *cocurrent*, *countercurrent*, and *cross-flow* are possible. Gillou et al. (2008) examined the effect of introducing H_2 at various points along the length of a microchannel reactor on the conversion of CO to hydrocarbons by the Fischer-Tropsch process. Compared to the introduction of H_2 along with CO at the inlet of the reactor, an increase in selectivity was obtained for some hydrocarbons.

1.5.1 Modelling, control, and optimization

A mathematical model of the reactor permits prediction of the conversion, selectivity (for systems with multiple reactions), flow patterns and *hot spots* or regions of high temperature. The effect of changes in operating conditions can also be examined. The availability of a model permits the development of suitable control schemes to ensure product quality, and also provides a valuable aid for the optimization of parameters or operating policies to satisfy specific objective functions. For example, Altinten et al. (2008) modelled a batch reactor used for the production of polystyrene. Using a suitable control scheme, the reactor temperature was varied with time so as to follow an "optimum" profile. This ensured that a polymer of the desired molecular weight was obtained in the minimum possible time.

2

Review of background material

2.1 Representation of reactions

The following notation will be used to represent irreversible and reversible reactions:

$$\begin{aligned} A + B &\rightarrow C \text{ irreversible} \\ A + B &\rightleftharpoons C \text{ reversible} \end{aligned} \tag{2.1}$$

Let A_i, $i = 1, N$ represent N species participating in a single reaction

$$a_1\,A_1 + a_2\,A_2 + ... \rightleftharpoons a_m\,A_m + ...a_N\,A_N$$

where a_i represents the number of moles of species A_i. The reaction can be written compactly as

$$\Sigma_{i=1}^{N} \nu_j\,A_j = 0$$

where ν_j is the *stoichiometric coefficient* for A_j. The usual convention is

$$v_j < 0,\ \text{ for reactants; } v_j > 0,\ \text{ for products}$$

For a reversible reaction, a species may be either a product or a reactant, depending on the direction in which the reaction proceeds. In such a case, the signs for the ν_i are chosen in the usual manner, i.e. assuming that the reaction proceeds from left to right. In case the reaction proceeds in the opposite direction, the expression for the reaction rate will change sign and the signs of the ν_j can be left unchanged.

The above notation can be readily extended to multiple reactions. If N species participate in M reactions, the reactions can be represented by

$$\sum_{j=1}^{N} \nu_{ij}\,A_j = 0,\ i = 1, M$$

where ν_{ij} is the stoichiometric coefficient for the j^{th} species participating in the i^{th} reaction.

2.2 The condition for reaction equilibrium

Consider an *isolated* system in which the reaction $A_1 + A_2 \rightleftharpoons A_3$ occurs. (An isolated system is one that does not interact with its surroundings. In particular, there is no transfer of heat, mass, or work between the system and the surroundings.) The second law of thermodynamics states that all changes or processes occurring in an isolated system must satisfy

$$\frac{\mathrm{d}S}{\mathrm{d}t} \geq 0 \tag{2.2}$$

where S is the total entropy of the system and t is the time. The system is said to be at an *equilibrium* state if

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 0$$

If we start with a binary mixture of A_1 and A_2, A_3 will be produced as the reaction proceeds. In accord with (2.2), S must either increase or remain constant. The expected variation of the entropy S and the molar concentration c_1 of A_1 with t is sketched in Fig. 2.1. The quantities S_e and C_{1e} represent the equilibrium values of S and C_1, respectively.

It follows from the above discussion that S is a *maximum* at an *equilibrium* state of an *isolated* system. In thermodynamics, an isolated system is defined as one that has a constant volume V and a constant internal energy U. Hence the equilibrium state corresponds to one that implies a maximum of S at constant U and V.

In reaction engineering, it is convenient to work with a *closed* system, rather than an isolated system. (A closed system is one that does not exchange mass with the surroundings.) We shall now derive the condition for the equilibrium state of a closed system in terms of a suitable thermodynamic quantities. The material below has been adapted from Denbigh (1971, p. 67-69).

Consider a closed system in contact with a heat reservoir that is maintained at a constant temperature T_r. Treating the system and the reservoir as an isolated compound system, the second law implies that

$$\Delta S + \Delta S_r \geq 0 \tag{2.3}$$

where ΔS and ΔS_r are the entropy changes of the system and the reservoir,

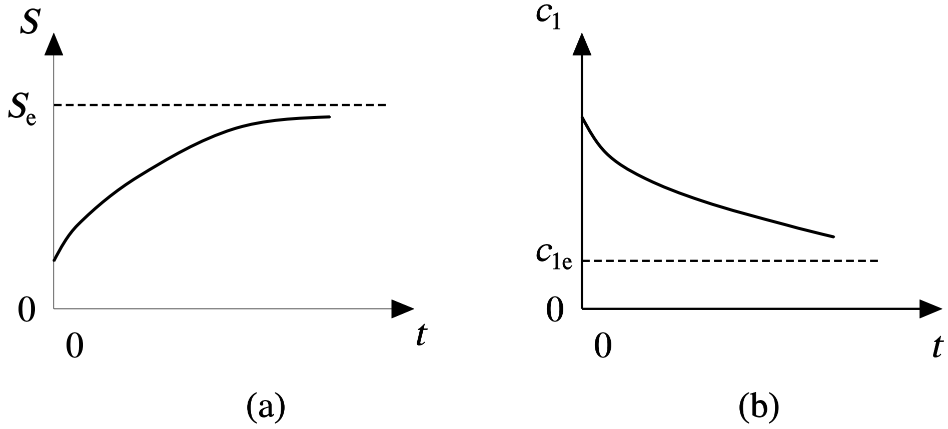

Fig. 2.1. Variation of the total entropy of the system S and the concentration of species 1 c_1 with the time t in an isolated system. The quantities S_e and c_{1e} represent the equilibrium values of S and c_1, respectively.

respectively. If ΔQ is the heat absorbed *by* the system *from* the reservoir, we have

$$\Delta S_r = -(\Delta Q)/T_r \tag{2.4}$$

regardless of whether the heat transfer is reversible or irreversible. The first law of thermodynamics implies that

$$\Delta U = \Delta Q - \Delta W \tag{2.5}$$

where ΔU is the change in internal energy of the *system* and ΔW is the work done *by* the system on the surroundings. Equations (2.3)-(2.5) imply that

$$T_r\,\Delta S - (\Delta U + \Delta W) \geq 0$$

or, adding and subtracting $\Delta(p\,V)$, where p is the pressure of the fluid

$$\Delta(U + p\,V - T_r\,S) \leq -\Delta W + \Delta(p\,V) \tag{2.6}$$

Consider a special case where the initial state 1 and the final state 2 of the system are such that (i) $T_1 = T_2 = T_r \equiv T$, and (ii) $p_1 = p_2 \equiv p$. Noting that the Gibbs free energy is defined by

$$G \equiv U + p\,V - T\,S \tag{2.7}$$

(2.6) reduces to

$$\Delta G|_{T,p} \leq -(\Delta W - p\,\Delta V) \equiv -\Delta W' \tag{2.8}$$

where $\Delta W'$ is the work done by the system, *excluding* that due to volume change. (For a *solid* phase, the work due to volume change is *not* given by $p\,\Delta V$. However, the final result (2.9) is unaltered (Callen, 1985, p. 305).)

If $\Delta W' = 0$, (2.8) reduces to

$$\Delta G|_{T,p} \leq 0 \tag{2.9}$$

Hence the Gibbs free energy G must either remain *constant* or *decrease* for all changes in a closed system maintained at constant T, p, and G must be a *minimum* at equilibrium.

In order to relate (2.9) to measurable quantities such as temperature, pressure, and composition, we use the *Gibbs equation.* For a single-phase system containing N species, the Gibbs equation is given by

$$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T + \sum_{i=1}^{N} \mu_i\,\mathrm{d}n_i \tag{2.10}$$

where

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,\,p,\,n_{j\neq i}} \tag{2.11}$$

is the *chemical potential* of species i, and n_i is the number of moles of species i.

Consider a single reaction occurring in a closed system containing a fluid, and assume that there are no *spatial* gradients. Then the *mass balances* are given by

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = V\,\nu_i\,\dot{r},\ \ i = 1, N \tag{2.12}$$

where V is the volume of the system and $\dot{r}$ is the *reaction rate* for this reaction. For fluid-phase systems, the usual dimensions of $\dot{r}$ are moles/unit volume/unit time. Even though there are N equations of the form (2.12), there is only one independent reaction. Hence, as suggested by de Donder (1922) (cited in Laidler, 2007, p. 7), all the $\{n_i\}$ can be expressed in terms of a variable ξ, called the *extent of reaction.* Let

$$n_i = n_{i0} + \nu_i\,\xi,\ \ i = 1, N \tag{2.13}$$

where n_{i0} is the *initial* (i.e. at time $t = 0$) number of moles of i. Equations (2.13) and (2.12) imply that

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = V\,\dot{r} \tag{2.14}$$

with the initial condition $\xi(0) = 0$.

Expressing the mole numbers in terms of the extent of reaction, (2.10) can be written as

$$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T + \sum_{i=1}^{N} \mu_i\,\nu_i\,\mathrm{d}\xi \tag{2.15}$$

As G must be a minimum at an equilibrium state of a closed system maintained at constant (T, p), we must have

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 0$$

or

$$\sum_{i=1}^{N} \mu_i\,\nu_i = 0 \tag{2.16}$$

and

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} > 0$$

or

$$\sum_{i=1}^{N} \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p} \nu_i > 0 \tag{2.17}$$

Equation (2.16) represents the condition for *reaction equilibrium.* It holds even if the system contains more than one phase, and the reaction involves components in *different* phases (Denbigh, 1971, p. 140).

The *affinity* of the reaction is defined by

$$\tilde{A} \equiv -\sum_{i=1}^{N} \mu_i \, \nu_i \tag{2.18}$$

Equation (2.15) implies that

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = -\tilde{A} \tag{2.19}$$

Hence if $\tilde{A} > 0$, G *decreases* as the extent of reaction ξ increases, and the reaction proceeds from *left to right.*

2.3 Models for the chemical potential

Equation (2.15) can be used to compute the equilibrium composition for a single reaction in a closed system, provided a model is available for the dependence of the chemical potentials $\{\mu_i\}$ on temperature T, pressure p, and composition. Some models are discussed briefly below. For more details, the reader is referred to Denbigh (1971, pp. 111-115, 125-126, 249, 270-271) and Smith et al. (2001, pp. 384, 390, 577).

(a) *The perfect gas mixture*

The *perfect gas mixture* is *defined* as one for which (Denbigh, 1971, p. 115)

$$\mu_i(T, p, \mathbf{y}) \equiv \mu_{i0}(T, p_0) + R\,T \, \ln\left(\frac{p\,y_i}{p_0}\right), \; i = 1, N \tag{2.20}$$

where $\mathbf{y}$ is the vector of $N-1$ independent mole fractions $y_i, i = 1,\, N-1$, μ_{i0} is the chemical potential of *pure* i at a temperature T and a *reference* pressure p_0, R is the gas constant, y_i is the mole fraction of species i, and p is the *total* pressure of the mixture. The use of (2.20) along with suitable thermodynamic relations leads to the following familiar results for a perfect gas mixture

$$p\,V = n\,R\,T; \;\; p_i \equiv p\,y_i = n_i\,R\,T/V, \;\; i = 1, N \tag{2.21}$$

where V is the volume occupied by the mixture, p_i is the partial pressure of

i, n_i is the number of moles of species i, and

$$n \equiv \sum_{i=1}^{N} n_i$$

is the total number of moles.

(b) *The ideal solution*

The *ideal solution* is defined by (Denbigh, 1971, p. 249)

$$\mu_i(T, p, \mathbf{y}) \equiv \mu_{i0}(T, p) + RT\ \ln(y_i),\ \ i = 1, N \tag{2.22}$$

where μ_{i0} is the chemical potential of *pure* i at (T, p). Equation (2.22) can be used for ideal gaseous, liquid, or solid solution.

(c) *The non-ideal solution*

To account for non-ideal behaviour, (2.22) is modified by introducing a variable γ_i, called the *activity coefficient*, such that (Denbigh, 1971, p. 270)

$$\mu_i(T, p, \mathbf{y}) \equiv \mu_{i0}(T, p) + RT\ \ln(\gamma_i\, y_i),\ \ i = 1, N \tag{2.23}$$

Note that μ_{i0} is *independent* of the composition, and the composition dependence of μ_i is accounted for solely by the term $\gamma_i\, y_i$. The value of μ_{i0} can be fixed by choosing a convention for γ_i. If all the species forming the solution remain in the *same phase* as the solution in their pure states at (T, p), the usual convention is

$$\gamma_i \to 1 \text{ as } y_i \to 1 \tag{2.24}$$

In this case, μ_{i0} is the chemical potential of pure i at (T, p).

Consider a liquid solution, and let $i = 1, m$ denote species that remain as liquids in their pure states at (T, p). The other species ($i = m{+}1, N$) are either gases or solids in their pure states at (T, p). Convention (2.24) applies to the first m species, and hence

$$\gamma_i \to 1 \ \text{ as } \ y_i \to 1,\ \ i = 1, m \tag{2.25}$$

For the other species, the usual convention is

$$\gamma_i \to 1 \text{ as } y_i \to 0,\ \ i = m + 1, N \tag{2.26}$$

For $i = m + 1, N$, μ_{i0} is the chemical potential of pure i in a hypothetical liquid state. It is a hypothetical state as pure i will not, by definition, be in a liquid state at (T, p).

Equation (2.23) can be used for gaseous, liquid, or solid solutions.

Additional details regarding the determination and use of activity coefficients may be found in Denbigh (1971, pp. 281-288), Prausnitz et al. (1999, pp. 222-236), and Sandler (2006, pp. 419-461).

Remarks

1. The *activity* of a species i is defined by Denbigh (1971, p. 287)

$$a_{i(y)} \equiv \gamma_i \, y_i \tag{2.27}$$

where the subscript y indicates that mole fractions are used as a measure of the composition of the mixture, and γ_i is the activity coefficient based on mole fractions. For some applications, it is convenient to replace y_i in (2.27) by some other measures of the composition, such as the molar concentration c_i or the *molality* $\hat{c}_i$. Here $\hat{c}_i$ is the number of moles of i per kg of the solvent. The molality is often used for electrolyte solutions (Prausnitz et al., 1999, p. 218).

Thus we have

$$\begin{aligned} a_{i(c)} &\equiv \frac{\gamma_{i(c)} \, c_i}{c_{i0}} \\ a_{i(\hat{c})} &\equiv \frac{\gamma_{i(\hat{c})} \, \hat{c}_i}{\hat{c}_{i0}} \end{aligned} \tag{2.28}$$

As the activity is a *dimensionless* quantity, (2.28) involve a *reference composition* characterized by c_{i0} or $\hat{c}_{i0}$. For ions and molecules dissolved in water, the usual reference composition is (Sawyer et al., 2003, p. 31, Sandler, 2006, p. 712)

$$c_{i0} = 1\,\mathrm{M} \ \text{(i.e. 1 mol/L)}, \ \hat{c}_{i0} = 1 \ \text{mol/kg of water} \tag{2.29}$$

For the *solvent*, and for *pure* liquids and solids in equilibrium with an aqueous solution, the usual reference state is the concentration or molality of the pure component

$$c_{i0} = c_{i,\,\mathrm{pure}}; \ \hat{c}_{i0} = \hat{c}_{i,\,\mathrm{pure}} \tag{2.30}$$

The conventions adopted for $\gamma_{i(c)}$ and $\gamma_{i(\hat{c})}$ are similar to those used for γ_i. For example, consider a liquid mixture and a solute i that is not a liquid at the same (T, p) as the solution. Then the convention is that

$$\gamma_{i(c)} \to 1 \ \text{as} \ c_i \to 0 \tag{2.31}$$

In terms of the activities, (2.23) can be rewritten as

$$\begin{aligned} \mu_i &\equiv \mu_{i0}(T,p) + R\,T \, \ln a_{i(y)} \qquad (2.32) \\ &\equiv \mu_{i0(c)}(T,p) + R\,T \, \ln a_{i(c)} \qquad (2.33) \end{aligned}$$

$$\equiv \quad \mu_{i0(\hat{c})}(T,p) + R\,T\,\ln a_{i(\hat{c})} \tag{2.34}$$

2. For *gas* mixtures, it is common practice to use fugacities instead of activity coefficients. Thus (2.23) can be rewritten as Denbigh (1971, p. 125)

$$\mu_i(T,p,\mathbf{y}) \equiv \mu_{i0}(T,p_0) + R\,T\,\ln\left(\frac{f_i}{f_{i0}}\right),\ i = 1, N \tag{2.35}$$

where f_i is the *fugacity* of species i and μ_{i0} and f_{i0} are the chemical potential and fugacity, respectively, of pure i at a temperature T and a reference pressure p_0. A common choice for f_{i0} is $f_{i0}(T,p_0) = 1$ atm, in which case p_0 is the pressure for which the fugacity of pure i is 1 atm. As noted by Denbigh (1971, p. 123), if $p \leq 1$ atm, $f_{i0} \approx p_0$ for most gases. Thus the choice $f_{i0} = 1$ atm implies that $p_0 \approx 1$ atm.

As in the case of (2.23), (2.35) can be used for gaseous, liquid, and solid solutions.

3. In accord with the experimental observation that the mixture should behave like a perfect gas mixture in the limit $p \to 0$, (2.20) and (2.35) imply that

$$\lim_{p\to 0} \frac{f_i}{f_{i0}} = \frac{p\,y_i}{p_0} \tag{2.36}$$

Thus the fugacity is *proportional* to the partial pressure $p_i \equiv p\,y_i$ at low pressures.

4. For an ideal solution, (2.22) and (2.35) imply that

$$R\,T\,\ln\left(\frac{f_i}{f_{i0}\,y_i}\right) = \mu_{i0}(T,p) - \mu_{i0}(T,p_0) \tag{2.37}$$

As the right hand side is independent of the composition, its value remains unchanged in the limit $y_i \to 1$. Hence (2.37) implies that

$$\frac{f_i}{f_{i0}\,y_i} = \lim_{y_i\to 1} \frac{f_i}{f_{i0}\,y_i} = \frac{f_{i,\text{pure}}}{f_{i0}}$$

or

$$f_i = f_{i,\text{pure}}\,y_i \tag{2.38}$$

Equation (2.38) is called the *Lewis and Randall rule.*

2.4 The equilibrium constant and the equilibrium composition

For a single reaction in a single phase system, the condition for reaction equilibrium is (see (2.17))

$$\sum_{i=1}^{N} \mu_i \, \nu_i = 0 \tag{2.39}$$

For a perfect gas mixture, (2.39) and (2.20) imply that

$$\sum_{i=1}^{N} \mu_{i0} \, \nu_i = -R\,T \, \ln \left[\prod_{i=1}^{N} \left(\frac{p_{ie}}{p_0} \right)^{\nu_i} \right] \tag{2.40}$$

where p_{ie} is the *equilibrium* value of the partial pressure p_i of species i. The *equilibrium constant* is defined by

$$K_p \equiv \prod_{i=1}^{N} \left(\frac{p_{ie}}{p_0} \right)^{\nu_i} = \prod_{i=1}^{N} \left(\frac{p \, y_{ie}}{p_0} \right)^{\nu_i} \tag{2.41}$$

where y_{ie} is equilibrium mole fraction of species i. Introducing the *standard Gibbs free energy change for the reaction*

$$\Delta G_0 \equiv \sum_{i=1}^{N} \mu_{i0}(T, p_)) \, \nu_i \tag{2.42}$$

(2.40) can be rewritten as

$$\Delta G_0 - R\,T \, \ln K_p \tag{2.43}$$

Equations (2.42) and (**??**) imply that K_p is *independent* of the pressure p and $K_p = K_p(T)$. This is true only for a perfect gas mixture. For a non-ideal gas mixture, K_p is still defined by (2.41), but (2.43) is not valid.

The *equilibrium* composition in a *closed* system at constant (T, p) can be calculated as follows. For ease of discussion, consider a perfect gas mixture. Using tables of thermodynamic properties, values of ΔG_0 can be calculated for most reactions. The value of K_p then follows from (2.43). As

$$y_{ie} = n_{ie}/n_e \tag{2.44}$$

where n_{ie} and n_e are the number of moles of species i and the total number of moles, respectively, at equilibrium, (2.41) can be rewritten as

$$K_p = \prod_{i=1}^{N} \left(\frac{p \, n_{ie}}{p_0 \, n_e} \right)^{\nu_i} \tag{2.45}$$

or using (2.13)

$$K_p = \prod_{i=1}^{N} \left[\left(\frac{p}{p_0} \right) \left(\frac{n_{i0} + \nu_i \, \xi_e}{n_0 + (\Delta\nu) \, \xi_e} \right) \right]^{\nu_i} \tag{2.46}$$

Here ξ_e is the extent of reaction at an equilibrium state, and $n_0 \equiv \sum_{i=1}^{N} n_i$ and $\Delta\nu \equiv \sum_{i=1}^{N} \nu_i$ are the total number of moles at the initial state and the change in the number of moles accompanying the reaction, respectively. Equation (2.46) represents a nonlinear equation for the extent of reaction ξ_e. Except in simple cases, the equation must be solved iteratively.

2.5 The effect of temperature on the equilibrium composition of a perfect gas mixture

Taking the logarithm of (2.45) and using (2.43), we obtain

$$-\frac{\Delta G_0}{R\,T} = \ln K_p = \sum_{i=1}^{N} \nu_i \, \ln \left(\frac{p \, n_{ie}}{p_0 \, n_e} \right) \tag{2.47}$$

Differentiating (2.47) with respect to T, and using (2.13), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}T} \left(-\frac{\Delta G_0}{R\,T} \right) = \frac{\mathrm{d}}{\mathrm{d}T} (\ln K_p) = \sum_{i=1}^{N} \left[\frac{\nu_i}{n_{ie}} \frac{\mathrm{d}n_{ie}}{\mathrm{d}\xi_e} - \frac{\nu_i}{n_e} \frac{\mathrm{d}n_e}{\mathrm{d}\xi_e} \right] \frac{\mathrm{d}\xi_e}{\mathrm{d}T} \tag{2.48}$$

Substituting for ΔG_0 from (2.42), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}T} \left(-\frac{\Delta G_0}{R\,T} \right) == -\sum_{i=1}^{N} \frac{\nu_i}{R} \frac{\mathrm{d}}{\mathrm{d}T} \left(\frac{\mu_{i0}}{T} \right) = \frac{\Delta H_0}{R\,T^2} \tag{2.49}$$

where

$$\Delta H_0 \equiv \sum_{i=1}^{N} \nu_i \, h_{i0} \tag{2.50}$$

is the *standard enthaply change for the reaction* and h_{i0} is the molar enthalpy of pure i at (T, p_0). Hence (2.48) reduces to *van't Hoff's* equation

$$\frac{\mathrm{d}}{\mathrm{d}T} (\ln K_p) = \frac{\Delta H_0}{R\,T^2} \tag{2.51}$$

As $n_i = n_i(\xi)$, (2.13) and (2.48) imply that

$$\frac{\mathrm{d}}{\mathrm{d}T} (\ln K_p) = \left[\sum_{i=1}^{N} \frac{\nu_i^2}{n_{ie}} - \frac{(\Delta\nu)^2}{n_e} \right] \frac{\mathrm{d}\xi_e}{\mathrm{d}T} \tag{2.52}$$

Using (2.52), (2.51) can be rewritten as

$$\frac{\Delta H_0}{RT^2} = \left[\sum_{i=1}^{N} \frac{\nu_i^2}{n_{ie}} - \frac{(\Delta\nu)^2}{n_e}\right] \frac{\mathrm{d}\xi_e}{\mathrm{d}T} \tag{2.53}$$

The Schwarz inequality (see, for example, Arfken and Weber, 2001, p. 607) can be used to show that the quantity in square brackets on the right hand side of (2.53) is always positive. Hence $\mathrm{d}\xi_e/\mathrm{d}T$ has the *same* sign as ΔH_0.

An *exothermic* reaction is defined as one for which $\Delta H_0 < 0$. In this case, $\mathrm{d}\xi_e/\mathrm{d}T < 0$, and hence the *equilibrium* extent of reaction *decreases* as T increases. If species i is a reactant, its *conversion* X_i, defined by

$$X_i \equiv \frac{n_{i0} - n_i}{n_{i0}} \tag{2.54}$$

is *directly proportional* to the extent of reaction ξ. Hence X_i also decreases as T increases. Conversely, for an *endothermic* reaction, the equilibrium conversion increases as T increases.

Remark Consider a chemical reaction in closed system, whose volume V changes suitably to maintain constant (T, p). If the state of the system changes from state 1 to state 2 as the reaction proceeds, the enthalpy change of the system is given by

$$\Delta H = \Delta U + \Delta(p\,V) = \Delta U + p\,\Delta V$$

or, using the first law of thermodynamics, and assuming that work is associated only with volume change

$$\Delta H = \Delta Q \tag{2.55}$$

where ΔQ is the heat absorbed by the system. Thus ΔH_0 is the heat absorbed by the system when the reactants are taken in stoichiometric proportions, with *each* reactant at (T, p_0), and are completely converted to products, with *each* product at (T, p_0) (Denbigh, 1971, p. 142).

2.6 The effect of pressure on the equilibrium composition of a perfect gas mixture

Differentiating (2.47) with respect to p, we obtain

$$\frac{\partial}{\partial p}(\ln K_p) = 0 = \left[\sum_{i=1}^{N} \frac{\nu_i^2}{n_{ie}} - \frac{(\Delta\nu)^2}{n_e}\right] \frac{\partial \xi_e}{\partial p} + \frac{\Delta\nu}{p}$$

or

$$\frac{\partial \xi_e}{\partial p} = -\frac{\Delta\nu}{p\left[\sum_{i=1}^{N}\frac{\nu_i^2}{n_{ie}} - \frac{(\Delta\nu)^2}{n_e}\right]} \tag{2.56}$$

If the reaction is accompanied by an *increase* in the number of moles, i.e., $\Delta\nu > 0$, (2.56) implies that $\partial\xi_e/\partial p < 0$. Hence the equilibrium conversion decreases as p increases. Conversely, if $\Delta\nu > 0$, the conversion increases as p increases.

Remark Equations (2.53) and (2.56) are quantitative expressions of *Le Chatelier's principle* (Atkins and de Paula, 2002, p. 234): "A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance."

2.7 Feasibility of reactions

As mentioned in section 2.2, a reaction proceeds from left to right if

$$\tilde{A} = -\sum_{i=1}^{N} \mu_i\,\nu_i > 0$$

The computation of $\tilde{A}$ requires a knowledge of T, p, and the composition. A *rough* idea of the direction in which the reaction is likely to occur may be obtained by calculating the standard free energy change for the reaction $\Delta G_0 = \sum_{i=1}^{N}\mu_{i0}(T,p_0)\,\nu_i$. Large *negative* values of ΔG_0 imply that the reaction is *promising*, i.e. it is likely to proceed from left to right. On the other hand, large *positive* values of ΔG_0 imply that the reaction is *not promising*, i.e. it is likely to proceed from right to left.

Equation (2.43) implies that if $\Delta G_0 \ll 0$, K_p is $\gg 1$. To understand the effect of K_p on the conversion, it is helpful to rewrite (2.46) as

$$\ln K_p = q \equiv \sum_{i=1}^{N}\nu_i\,[\ln(n_{i0}+\nu_i\,\xi_e) - \ln(n_0+(\Delta\nu)\,\xi_e)] + (\Delta\nu)\,\ln(p/p_0) \tag{2.57}$$

At a fixed value of p, if K_p increases, (2.57) implies that ξ_e increases, as $\partial q/\partial\xi_e > 0$. Conversely, if $K_p \ll 1$, we may expect ξ_e to be small. However, if the initial mixture contains only the reactants, the equilibrium value of ξ_e will be small but non-zero even if $\Delta G_0 \gg 0$.

Dodge (1944) has listed the following thumb rules: (a) if ΔG_0 (298 K, 1 atm) < 0, the reaction is promising, (b) if $0 < \Delta G_0 < 40$ kJ/mol, a more detailed examination is warranted, and (c) if $\Delta G_0 > 40$ kJ/mol, the reaction is very unlikely. For example, consider the synthesis of NO from N_2 and O_2. For this reaction, $\Delta G_0 = 86.6$ kJ/mol of NO, whereas for the synthesis of NH_3 by the reaction

$$\frac{1}{2}\,\mathrm{N_2\,(g)} + \frac{3}{2}\,\mathrm{H_2\,(g)} \rightleftharpoons \mathrm{NH_3\,(g)} \tag{2.58}$$

$\Delta G_0 = -17$ kJ/mol of NH_3. Hence the thumb rules suggest that very little NO will be formed.

2.8 Reaction equilibrium in an imperfect gas mixture

Using the model (2.35) for the chemical potential and the condition for reaction equilibrium (2.16), we obtain

$$\sum_{i=1}^{N} \mu_i\,\nu_i = 0$$

or

$$R\,T\,\ln K_f = -\Delta G_0(T, p_0) \tag{2.59}$$

where

$$K_f \equiv \prod_{i=1}^{N} \left(\frac{f_{ie}}{f_{i0}}\right)^{\nu_i} \tag{2.60}$$

is the equilibrium constant based on fugacities and f_{ie} is the equilibrium value of the fugacity of species i.

For an imperfect gas mixture, it is K_f and not K_p that is *independent* of the pressure p. This point is illustrated by the data of Larson and Dodge (cited in Denbigh, 1971, p. 152). As p increases from 10 atm to 300 atm, K_p increases by 34 % of the smaller value, whereas K_f increases by only 1.5 %. The small variation of K_f occurs because of the errors introduced by using the Lewis and Randall rule (2.38) to estimate the fugacities $\{f_i\}$. For $p > 300$ atm, the variation of K_f is more pronounced.

2.9 Reaction equilibrium in a liquid mixture

If (2.23) is used as a model for the chemical potential, (2.39)implies that

$$\sum_{i=1}^{N} \mu_{i0}\,\nu_i = -R\,T\,\ln K_\gamma\,K_y \tag{2.61}$$

where

$$K_\gamma \equiv \prod_{i=1}^{N} \gamma_i^{\nu_i};\ K_y \equiv \prod_{i=1}^{N} y_i^{\nu_i} \tag{2.62}$$

Equation (2.61) can be used to calculate the equilibrium composition provided the values of the $\{\mu_{i0}\}$ are known. For solutes that are not liquids at the same (T, p) as the solution, (2.26), (2.27), and (2.32) imply that μ_{i0} is the chemical potential of *pure* i in a hypothetical liquid state. However, the values tabulated for such solutes often correspond to a hypothetical ideal solution of unit molality. In such cases, activities defined on the molality scale may be used. Equations (2.34) and (2.29) imply that $\mu_{i0(\hat{c})}(T, p)$ is the chemical potential of i in a hypothetical ideal solution of unit molality. Further, as noted by Denbigh (1971, p. 294), the effect of pressure on the liquid and solid phases may usally be neglected, unless it is very high compared to the standard pressure $p_0 = 1$ atm. Hence

$$\mu_{i0(\hat{c})}(T, p) \approx \mu_{i0(\hat{c})}(T, p_0) \tag{2.63}$$

and the tabulated value of the standard Gibbs free energy of formation of i may be used for $\mu_{i0(\hat{c})}(T, p)$.

2.10 Reaction equilibrium in systems involving multiple phases

Consider the thermal decomposition of caclium carbonate (Denbigh, 1971, p. 156)

$$\mathrm{CaCO_3\,(s)} \rightleftharpoons \mathrm{CaO\,(s)} + \mathrm{CO_2\,(g)} \tag{2.64}$$

The partial pressure of CO_2, p_{CO_2} can be related to the standard Gibbs free energy change for the reaction as follows.

The condition for reaction equilibrium is

$$-\mu_{\mathrm{CaCO_3}}\,(\mathrm{s}) + \mu_{\mathrm{CaO}}\,(\mathrm{s}) + \mu_{\mathrm{CO_2}}\,(\mathrm{g}) = 0 \tag{2.65}$$

Assuming that both $CaCO_3\,(s)$ and $CaO\,(s)$ have negligible vapour pressures, only CO_2 will be present in the vapour phase. Treating it as a perfect gas, we have

$$\mu_{\mathrm{CO_2}}\,(\mathrm{g}) = \mu_{0,\mathrm{CO_2}}(T, p_0) + RT\,\ln(p_{\mathrm{CO_2}}/p_0) \tag{2.66}$$

Using (2.66), (2.67) reduces to

$$-\mu_{\mathrm{CaCO_3}}\,(\mathrm{s}) + \mu_{\mathrm{CaO}}\,(\mathrm{s}) + \mu_{0,\mathrm{CO_2}}\,(\mathrm{g}) = -RT\,\ln(p_{\mathrm{CO_2}}/p_0) \tag{2.67}$$

To proceed further, we assume that $CaCO_3\,(s)$ and $CaO\,(s)$ form *immiscible* solid phases, i.e. a phase contains either pure $CaCO_3$ or pure CaO. (The case where two solids are miscible and form a mixture or *solid solution* is discussed in Sandler (2006, pp. 679-687).) Then $\mu_{\mathrm{CaCO_3}}$ and μ_{CaO} depend only on (T, p). For a pure phase, $\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p$, where s and v are the molar entropy and the molar volume, respectively, of the material. Considering CaO and assuming that v_{CaO} is approximately independent of p, we obtain

$$\mu_{\mathrm{CaO}}(T,p) = \mu_{\mathrm{CaO}}(T,p_0) + v_{\mathrm{CaO}}\,(p - p_0) \tag{2.68}$$

Using a similar expression for $\mu_{\mathrm{CaCO_3}}$,

$$\begin{aligned}&\mu_{0,\mathrm{CaO\,(s)}}(T,p_0) + \mu_{0,\mathrm{CO_2\,(g)}}(T,p_0) - \mu_{0,\mathrm{CaCO_3\,(s)}}(T,p_0)\\ &+(v_{\mathrm{CaO\,(s)}} - v_{\mathrm{CaCO_3\,(s)}})\,(p - p_0) = -RT\,\ln(p_{\mathrm{CO_2}}/p_0)\end{aligned} \tag{2.69}$$

As

$$\Delta G_0 = \mu_{0,\mathrm{CaO\,(s)}}(T,p_0) + \mu_{0,\mathrm{CO_2\,(g)}}(T,p_0) - \mu_{0,\mathrm{CaCO_3\,(s)}}(T,p_0) \tag{2.70}$$

(2.69) reduces to

$$\Delta G_0 + (v_{\mathrm{CaO\,(s)}} - v_{\mathrm{CaCO_3\,(s)}})\,(p - p_0) = -RT\,\ln(p_{\mathrm{CO_2}}/p_0) \tag{2.71}$$

The second term on the left hand side of (2.71) is usually negligible compared to the first term. For example, $\Delta G_0(298K, 1\mathrm{atm}) = 135$ kJ/mol, whereas $(v_{\mathrm{CaO\,(s)}} - v_{\mathrm{CaCO_3\,(s)}})\,(p - p_0) \approx 0.2$ kJ/mol for $p - p_0 = 100$ atm. Hence (2.71) may be approximated as

$$\Delta G_0 \approx -RT\,\ln(p_{\mathrm{CO_2}}/p_0) \tag{2.72}$$

By analogy with (2.41), we may define a *partial equilibrium constant*

$$K_p' \equiv \frac{p_{\mathrm{CO_2}}}{p_0} \tag{2.73}$$

Equation (2.72) permits evaluation of the pressure of CO_2 (g) that is in *equilibrium* with $CaCO_3$ (s) and CaO (s). As noted by Denbigh (1971, p. 158), if $p_{\mathrm{CO_2}}/p_0 > K_p'$, CaO will be converted to $CaCO_3$.

Another example involving gaseous and liquid phases is given by the formation of urea by the reaction (Denbigh, 1971, p. 294)

$$\mathrm{CO_2(g)} + 2\,\mathrm{NH_3} \rightleftharpoons \mathrm{CO(NH_2)_2(aq)} + \mathrm{H_2O} \tag{2.74}$$

Numbering the species from left to right in the above equation as 1-4, the values reported in the literature for the standard free energies of formation are, in kJ/mol

$$\mu_{10} = -394.4,\ \mu_{20} = -16.64,\ \mu_{30(\hat{c})} = -203.8,\ \mu_{40(y)} = -237.2 \tag{2.75}$$

Hence the standard free energy change for the reaction (2.75) is

$$\Delta G_0 \equiv \mu_{40(y)} + \mu_{30(\hat{c})} - 2\,\mu_{20} - \mu_{10} = -13.32 \text{ kJ/mol} \tag{2.76}$$

and the condition for reaction equilibrium is

$$\Delta G_0 = -RT\,\ln\left[\frac{\gamma_4\,x_4\,\gamma_{3(\hat{c})}\,(\hat{c}_3/\hat{c}_{30})}{(f_2/f_{20})^2\,(f_1/f_{10})}\right] \tag{2.77}$$

2.11 Systems with multiple reactions

The discussion will be confined to a single phase system containing N species participating in M reactions. For example. the following reactions occur during the production of formaldehyde (HCHO) from methanol (CH_3OH):

$$\begin{aligned} CH_3OH &\rightleftharpoons HCHO + H_2 \\ CH_3OH + \frac{1}{2}O_2 &\rightleftharpoons HCHO + H_2O \\ HCHO &\rightleftharpoons CO + H_2 \\ HCHO + \frac{1}{2}O_2 &\rightleftharpoons CO + H_2O \\ CO + \frac{1}{2}O_2 &\rightleftharpoons CO_2 \end{aligned} \tag{2.78}$$

We could also add the reaction

$$CH_3OH \rightleftharpoons CO + 2\,H_2$$

but it is not an independent reaction, as it can be obtained by adding the first and the third reactions in (2.78).

It is useful to calculate the number of *stoichiometrically independent* reactions N_R. The value of N_R permits examination of a system involving N_R reactions, rather than the original system of $M \geq N_R$ reactions. A method for calculating N_R is explained below.

Consider the system of reactions

$$\sum_{j=1}^{N} \nu_{ij}\,A_j = 0,\ \ i = 1, M \tag{2.79}$$

where ν_{ij} is the stoichiometric coefficient for the j^{th} species in the i^{th} reaction. Let the *stoichiometric matrix* $[\boldsymbol{\nu}]$ be defined by

$$[\boldsymbol{\nu}] = [\nu_{ij}] \tag{2.80}$$

Thus the element in the i^{th} row and j^{th} column of $[\boldsymbol{\nu}]$ is ν_{ij}. The number of stoichiometrically independent reactions is given by

$$N_R = \text{rank}([\boldsymbol{\nu}]) \tag{2.81}$$

Here the *rank* of $[\ \boldsymbol{\nu}]$ is the maximum number of *linearly independent* rows or columns of $[\ \boldsymbol{\nu}]$ (Kreyszig, 1993, p. 356-357); it can be found by *Gaussian elimination* or *Gauss elimination*, as discussed in Aris (1999, p. 13) and in books on numerical analysis (see, for example, Gerald and Wheatley, 1994, pp. 113-115). The following example is taken from Aris (1999, pp. 13-14).

Consider the reactions involved in the formation of hydrogen bromide (HBr):

$$\begin{aligned}
\mathrm{Br_2} &\rightarrow 2\,\mathrm{Br} \\
\mathrm{Br} + \mathrm{H_2} &\rightarrow \mathrm{HBr} + \mathrm{H} \\
\mathrm{H} + \mathrm{Br_2} &\rightarrow \mathrm{HBr} + \mathrm{Br} \\
\mathrm{H} + \mathrm{HBr} &\rightarrow \mathrm{H_2} + \mathrm{Br} \\
2\,\mathrm{Br} &\rightarrow \mathrm{Br_2}
\end{aligned} \tag{2.82}$$

The stoichiometric matrix is given by

$$\boldsymbol{\nu} = \begin{bmatrix} -1 & 2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ -1 & 1 & 0 & 1 & -1 \\ 0 & 1 & 1 & -1 & -1 \\ 1 & -2 & 0 & 0 & 0 \end{bmatrix}$$

The procedure is as follows.

(i) Rearrange the rows if necessary, so that the *pivot* $\nu_{11} \neq 0$. In the present example, rearrangement is not required.

(ii) Divide the first row by ν_{11} so that the first row is now given by $\nu_{1j} = [1\ -2\ 0\ 0\ 0]$.

(iii) Using row operations, i.e. forming linear combinations of the other rows with the first row, make all the elements in the first column (except ν_{11}) equal to zero. Thus we obtain

$$\boldsymbol{\nu}' = \begin{bmatrix} 1 & -2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ 0 & -1 & 0 & -1 & 1 \\ 0 & 1 & 1 & -1 & -1 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

(iv) Repeat steps 1-3, starting with ν_{22} as the pivot, and reducing $\nu_{i2}, i = 3, N$ to zero. The result is

$$\boldsymbol{\nu} = \begin{bmatrix} 1 & -2 & 0 & 0 & 0 \\ 0 & 1 & 1 & -1 & -1 \\ 0 & 0 & 1 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

As all the elements in the 3rd and 4th rows are zero, the process can be stopped at this stage. The rank of $\boldsymbol{\nu}$ is 3, the number of non-zero rows. Hence (2.81) implies that the number of stoichiometrically independent reactions is $N_R = 3$ in the present example.

2.12 Degrees of freedom for reactive systems

Suppose there are N species, P phases, and N_R independent chemical reactions. At an *equilibrium* state, the following conditions hold (Denbigh, 1971, p. 187):

$$T_j = T_1;\ p_j = p_1;\ \mu_{ji} = \mu_{1i},\ \ j = 2, P; i = 1, N \tag{2.83}$$

Here T_j and p_j are the temperature and pressure, respectively, of phase j and μ_{ji} is the chemical potential of species i in phase j. In addition, there are N_R conditions of reaction equilibrium, given by

$$\sum_{i=1}^{N} \nu_{li}\, \mu_{1i} = 0;\ l = 1, N_R \tag{2.84}$$

Equations (2.83) and (2.84) constrain the values of the independent intensive variables T_i, $p_i. i = 1, N$ and the mole fractions y_{ji}, $j = 1, P$, $i = 1, N - 1$. Here y_{ji} is the mole fraction of species i in phase j. Hence the number of *degrees of freedom* F, i.e. the excess of the number of variables over the number of constraints, is given by

$$F = (N - N_R) - P + 2 \tag{2.85}$$

In the absence of chemical reactions, $N_R = 0$. Hence (2.85) reduces to the familiar *phase rule*.

In a solution containing electrolytes, the requirement of electrical neutrality leads to an equation relating the concentrations of the ions. Hence the value of F is reduced by unity, as discussed in Denbigh (1971, p. 188).

2.13 Notation for reaction kinetics

Let $\dot{r}_i$ denote the *molar reaction rate* for species i, i.e. the moles of *i produced* per unit volume per unit time. For a single reaction, it is convenient to introduce an *intrinsic molar reaction rate* $\dot{\beta}$, such that

$$\dot{r}_i = \nu_i \, \dot{\beta} \tag{2.86}$$

Similarly, for multiple reactions we set

$$\dot{r}_i = \sum_{j=1}^{N_R} \nu_{ji} \, \dot{\beta}_j \tag{2.87}$$

where ν_{ji} is the stoichiometric coefficient for species i in reaction j, $\dot{\beta}_j$ is the intrinsic molar reaction rate for reaction j , and N_R is the number of stoichiometrically independent reactions.

2.14 Elementary reactions and reaction mechanisms

The reaction

$$A_1 + A_2 \rightarrow A_3 \tag{2.88}$$

is said to be an *elementary* reaction if a molecule of A_3 is formed by *direct* interaction or collision between one molecule of A_1 and one molecule of A_2. The *molecularity* of an elementary reaction is the number of *reactant* molecules participating in the reaction. Thus, for an elementary reaction of the form (2.88), the molecularity is 2.

If the molecules of A_1 and A_2 move independently, the probability of finding one molecule of A_1 and one molecule of A_2 at a given (macroscopic) location is proportional to $c_1 \, c_2$, where c_i is the molar concentration of A_i. Thus it may be expected that

$$\dot{\beta} \propto c_1 \, c_2 \tag{2.89}$$

for the reaction (2.88). This assumption may break down if there are strong long-range interactions between A_1 and A_2. Even if such interactions are ignored, (2.89) does not guarantee that (2.88) is an elementary reaction. For example, consider the gas-phase reaction

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)} \tag{2.90}$$

It was found that

$$\dot{\beta} \propto c_{\mathrm{H_2}}\, c_{\mathrm{I_2}} \tag{2.91}$$

for the forward reaction and

$$\dot{\beta} \propto c_{\mathrm{HI}}^2 \tag{2.92}$$

for the reverse reaction. Hence it was assumed till the early 1930's that (2.90) represented an elementary reaction. Subsequent work showed that other mechanisms were also involved, depending on the temperature and other conditions (Laidler, 2007, pp. 298-300). For example, iodine atoms may be involved in some cases. Thus the reaction rate for (2.90) is consistent with the assumption that it is elementary reaction, even though it is not.

A *non-elementary* reaction is one which proceeds by a sequence of elementary reactions. The sequence is called the *reaction mechanism.* Given a mechanism, the rate expression can be derived for a non-elementary reaction. The success of the postulated mechanism depends partly on the degree of agreement between the predicted and observed reaction rates. In some cases, as for the reaction (2.90), several different mechanisms may lead to the *same* rate expression. More information is then required to discriminate between rival mechanisms.

An example of a non-elementary reaction is provided by the reaction

$$\mathrm{H_2\,(g) + Br_2\,(g) \rightleftharpoons 2\,HBr\,(g)} \tag{2.93}$$

Bodenstein and Lind (1907) (cited in Laidler, 2007, p. 291 found that

$$\dot{\beta} = \frac{k\, c_{\mathrm{H_2}} \sqrt{c_{\mathrm{Br_2}}}}{1 + c_{\mathrm{HBr}}/(m\, c_{\mathrm{Br_2}})} \tag{2.94}$$

where k and m are constants. The mechanism for this reaction was suggested almost simultaneously by Christiansen (1919), Herzfeld (1919) and Polanyi (1920) (all cited in Laidler, 2007, p. 291). The steps involved are

$$\begin{array}{rcl}
\mathrm{Br_2} \rightarrow & \mathrm{2\,Br} & \text{initiation} \\
\mathrm{Br + H_2} \rightarrow & \mathrm{HBr + H} & \text{propagation} \\
\mathrm{H + Br_2} \rightarrow & \mathrm{HBr + Br} & \text{''} \\
\mathrm{H + HBr} \rightarrow & \mathrm{H_2 + Br} & \text{''}
\end{array}$$

$$\mathrm{Br} + \mathrm{Br} \rightarrow \qquad \mathrm{Br_2} \qquad \text{termination} \tag{2.95}$$

Using suitable assumptions, the mechanism (2.95) leads to a rate expression that is identical in form to the observed rate expression (2.94). The initiation, propagation, and termination steps are characteristic of *chain reactions*. Equation (2.95) involves the *free radicals* H and Br. (A free radical is an atom or group of atoms having an unpaired electron (Morrison and Boyd, 2002, p. 47).)

2.15 Rate expressions for homogeneous irreversible reactions

No reaction is truly irreversible, but under certain operating conditions, the concentrations of the reactants may be negligible at an equilibrium state. In such cases, the reaction is treated as an irreversible reaction. Some examples of reactions which must be treated as reversible reactions under industrial operating conditions are SO_2 oxidation and the synthesis of NH_3.

For a homogeneous fluid-phase reaction involving N species, the intrinsic reaction rate has the form

$$\dot{\beta} = \dot{\beta}(T, p, \mathbf{x}) \tag{2.96}$$

where T is the absolute temperature, p is the total pressure, and $\mathbf{x}$ is the vector of *independent* mole fractions with components $x_i, i = 1, N-1$. Equation (2.96) can be rewritten as

$$\dot{\beta} = \dot{\beta}(T, p, \mathbf{c}') \tag{2.97}$$

or

$$\dot{\beta} = \dot{\beta}(T, \mathbf{c}) \tag{2.98}$$

where $\mathbf{c}'$ is a vector of molar concentrations with components $c_1, i = 1, N-1$ and $\mathbf{c}$ is the vector with components $c_i, i = 1, N$. As an *equation of state* $f(T, p, \mathbf{c}) = 0$ relates T, p, and $\mathbf{c}$, only $N + 1$ of these variables are independent.

2.15.1 Special cases

(a) *Power law kinetics*

The intrinsic reaction rate is given by

$$\dot{\beta} = k(T) \prod_{i=1}^{N} c_i^{q_i} \tag{2.99}$$

where q_i is the *order* of the reaction with respect to the ith species. The *overall order* of the reaction is given by

$$q = \sum_{i=1}^{N} q_i \tag{2.100}$$

The function $k(T)$ is independent of the concentration, and hence is called the *rate constant.*

As an example, consider the thermal cracking of propane (C_3H_8) in the gas phase. A kinetic model proposed by Sundaram and Froment (1977) involves nine reactions, three of which are listed below along with rate expressions for the intrinsic reaction rates β_i.

$$C_3H_8 \;\rightarrow\; C_2H_4 + CH_4;\; \dot{\beta} = k_1\, c_{C_3H_8} \tag{2.101}$$

$$C_3H_8 \;\rightleftharpoons\; C_3H_6 + H_2;\; \dot{\beta} = k_2\, c_{C_3H_8} - k_2'\, c_{C_3H_6}\, c_{H_2} \tag{2.102}$$

$$2\, C_3H_6 \;\rightarrow\; 3\, C_2H_4;\; \dot{\beta} = k_3\, c_{C_3H_6} \tag{2.103}$$

The above reactions are approximations to a more realistic scheme involving free radicals. Equations (2.102) and (2.103) are first order irreversible reactions, whereas (2.103) is a reversible reaction of mixed order. At 800 °C, the values of the rate constants in s^{-1} are $k_1 = 2.34$, $k_2 = 2.12$, and $k_3 = 0.72$.

In (2.99), if $q_i < 0$ for a product, the reaction is said to be *product-inhibited.* This terminology is not restricted to power law kinetics, but is used whenever an increase in the product concentration decreases the reaction rate. For example, (2.94) shows that the forward reaction is inhibited by HBr. If $q_i = 0$ for a *reactant* A_i, the reaction is said to be *zero order* in A_i. This condition is likely to hold when A_i is present in a large excess compared to the other reactants, but it will break down at low concentrations.

(b) *Mass action kinetics*

The reaction

$$q_1\, A_1 + q_2\, A_2 \rightarrow q_3 \tag{2.104}$$

is said to follow *mass action* kinetics if the intrinsic reaction rate is given by (Guldberg and Waage, 1864, cited in Laidler, 2007, p. 2)

$$\dot{\beta} = k(T)\, c_1^{q_1}\, c_2^{q_2} \tag{2.105}$$

(c) *Michaelis-Menten kinetics*

These kinetics are often used to describe reactions catalyzed by enzymes. (An *enzyme* is usually a protein of high molecular weight, between

15,000 and several million daltons (Shuler and Kargi, 2004, p. 57). A dalton is the mass of a H atom, i.e. 1.66×10^{-27} kg.) For example, the enzyme urease catalyzes the hydrolysis of urea ($CO(NH_2)_2$) (Laidler, 2007, p. 399)

$$\mathrm{CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2\,NH_3} \tag{2.106}$$

For a *single* reactant or *substrate* S (in addition to water) that is converted to a product or products P by an enzyme E, the reaction is

$$S \overset{\mathrm{E}}{\rightarrow} P \tag{2.107}$$

Henri (1902) (cited in Kooijman, 2001) and Michaelis and Menten (1913) postulated the following mechanism (Shuler and Kargi, 2004, p.60)

$$\mathrm{E + S \rightleftharpoons ES \rightarrow E + P} \tag{2.108}$$

where ES denotes an *enzyme-substrate complex*. Assuming that the reversible reaction was at equilibrium, Henri (1902) and Michaelis and Menten (1913) showed that for an ideal batch reactor, the rate of production of the product was given by

$$\dot{\beta}_P = \frac{k\, c_{E_0}\, c_S}{k_m + c_S} \tag{2.109}$$

where $c_{E_0} = c_E + c_S$ is the initial concentration of the enzyme. Equation (2.109) represents *Michaelis-Menten* kinetics, but it is not clear why Henri's name is usually not included.

Rate expressions similar to (2.109) are also used when gaseous reactants are catalyzed by a solid catalysts. These are discussed in section 2.18.5.

2.16 Rate expressions for homogeneous reversible reactions

Consider the reaction

$$m_1\, A_1 + m_2\, A_2 \rightleftharpoons m_3\, A_3 + m_4\, A_4 \tag{2.110}$$

If (2.110) follows power law kinetics, the intrinsic reaction rate is given by

$$\dot{\beta} = k_f(T) \prod_1^N c_j^{q_j} - k_b(T) \prod_1^N c_j^{q_j{}'} \tag{2.111}$$

where k_f and k_b are the rate constants for the forward and backward reactions and the $\{q_j\}$ and $\{q_j'\}$ are constants. If (2.110) follows mass action kinetics, the reaction rate is given by

$$\dot{\beta} = k_f(T)\, c_1^{m_1}\, c_2^{m_2} - k_b(T)\, c_3^{m_3}\, c_4^{m_4} \tag{2.112}$$

2.17 Thermodynamic consistency of the rate expressions for reversible reactions

For the reaction (2.110), the condition for reaction equilibrium in a closed system at constant (T, p) is

$$m_3\, \mu_3 + m_4\, \mu_4 - m_1\, \mu_1 - m_2\, \mu_2 = 0 \tag{2.113}$$

Considering a perfect gas mixture, (2.20) and (2.113) imply that

$$K_p(T) \equiv \left(\frac{\tilde{p}_{3e}^{m_3}\, \tilde{p}_{4e}^{m_4}}{\tilde{p}_{1e}^{m_1}\, \tilde{p}_{2e}^{m_2}} \right) = \left(\frac{\tilde{c}_{3e}^{m_3}\, \tilde{c}_{4e}^{m_4}}{\tilde{c}_{1e}^{m_1}\, \tilde{c}_{2e}^{m_2}} \right) \left(\frac{c_*\, RT}{p_0} \right)^{\Delta m} \tag{2.114}$$

where

$$\tilde{p}_{ie} \equiv p_{ie}/p_0;\;\; \tilde{c}_{ie} \equiv c_{ie}/c_*;\;\; \Delta m \equiv m_3 + m_4 - m_1 - m_2 \tag{2.115}$$

p_{ie} and c_{ie} are the equilibrium values of the partial pressure and molar concentration, respectively, of species i, and p_0 and c_* are the reference pressure and the reference concentration, respectively.

The equilibrium constant based on concentrations K_c is defined by

$$K_c \equiv \left(\frac{\tilde{c}_{3e}^{m_3}\, \tilde{c}_{4e}^{m_4}}{\tilde{c}_{1e}^{m_1}\, \tilde{c}_{2e}^{m_2}} \right) \tag{2.116}$$

or for a general reaction by

$$K_c \equiv \prod_{i=1}^{N} \tilde{c}_{ie}^{\nu_i} \tag{2.117}$$

Note that K_c is dimensionless. In some books (see, for example, Schmidt, 2005, p. 35), K_c appears to be a dimensional quantity, but is not, as c_* has been chosen as unity in the same units as the $\{c_i\}$. Equations (2.116) and (2.117) imply that

$$K_p = K_c \left(\frac{c_*\, RT}{p_0} \right)^{\Delta m} \tag{2.118}$$

Hence $K_c = K_c(T)$.

If the reaction follows power law kinetics, (2.111) holds. As $\dot{\beta} = 0$ at equilibrium, we have

$$\frac{k_f}{k_b} = \frac{\prod_{i=1}^{N} c_{ie}^{q_j'}}{\prod_{i=1}^{N} c_{ie}^{q_i}} \tag{2.119}$$

For the reaction (2.110), (2.119) reduces to

$$\frac{k_f}{k_b} = \tilde{c}_{1e}^{q_1'-q_1}\, \tilde{c}_{2e}^{q_2'-q_2}\, \tilde{c}_{3e}^{q_3'-q_3}\, \tilde{c}_{4e}^{q_4'-q_4}\, c_*^{\Delta q} \tag{2.120}$$

where

$$\Delta q \equiv \sum_{i=1}^{4} (q_i' - q_i) \tag{2.121}$$

Equation (2.120) may be compared with (2.116), which can be rewritten as

$$K_c = \tilde{c}_{3e}^{m_3}\, \tilde{c}_{4e}^{m_4}\, \tilde{c}_{1e}^{-m_1}\, \tilde{c}_{2e}^{-m_2} \tag{2.122}$$

As noted by Denbigh (1971, pp. 444-445), both k_f/k_b and K_c are functions of the temperature T. Hence the right hand side of (2.120) must be a function of the right hand side of (2.122), i.e.

$$\tilde{c}_{1e}^{q_1'-q_1}\, \tilde{c}_{2e}^{q_2'-q_2}\, \tilde{c}_{3e}^{q_3'-q_3}\, \tilde{c}_{4e}^{q_4'-q_4}\, c_*^{\Delta q} = f(\tilde{c}_{3e}^{m_3}\, \tilde{c}_{4e}^{m_4}\, \tilde{c}_{1e}^{-m_1}\, \tilde{c}_{2e}^{-m_2}) \tag{2.123}$$

For a batch reactor, the equilibrium concentrations $\{c_{ie}\}$ can be varied by varying the initial composition of the reaction mixture. Hence (2.123) must hold for arbitrary values of the $\{c_{ie}\}$. It can be shown that (2.123) can be satisfied by requiring that $f(x) = x^n$, where n is a positive constant (Blum and Luus, 1964). Hence

$$\frac{q_3' - q_3}{m_3} = \frac{q_4' - q_4}{m_4} = \frac{q_1' - q_1}{-m_1} = \frac{q_2' - q_2}{-m_2} = n \tag{2.124}$$

If (2.124) holds, (2.116) and (2.120) imply that

$$\frac{k_f}{k_b} = K_c^n\, c_*^{\Delta q} \tag{2.125}$$

For a perfect gas mixture involving a reaction following power law kinetics, (2.124) ensures that the rate expression is *thermodynamically consistent*. For example, consider the production of phosgene ($COCl_2$) by the reaction

$$\mathrm{CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)} \tag{2.126}$$

The reaction rate is given by (Denbigh and Turner, 1972, p. 21)

$$\dot{\beta} = k_f \, c_{\mathrm{C}_0} \, c_{\mathrm{Cl}_2}^{3/2} - k_b \, c_{\mathrm{COCl}_2} \, c_{\mathrm{Cl}_2}^{1/2} \tag{2.127}$$

Equation (2.127) implies that

$$\begin{aligned} \frac{k_f}{k_b} &= \frac{c_{\mathrm{COCl}_2} \, c_{\mathrm{Cl}_2}^{1/2}}{c_{\mathrm{C}_0} \, c_{\mathrm{Cl}_2}^{3/2}} \\ &= \frac{\tilde{c}_{\mathrm{COCl}_2}}{\tilde{c}_{\mathrm{C}_0} \, \tilde{c}_{\mathrm{Cl}_2}} \, c_*^{-1} = K_c \, c_*^{-1} \end{aligned} \tag{2.128}$$

Hence (2.127) is thermodynamically consistent.

2.18 Theories for the rates of elementary reactions

The temperature dependence of the rate constant k is usually fitted by the *Arrhenius equation* (Arrhenius, 1899) (cited in Laidler, 2007, p. 42)

$$k = Ae^{-\frac{E}{RT}} \tag{2.129}$$

where the *pre-exponential factor* A and the *activation energy* E are treated as constants and T is the absolute temperature. van't Hoff (1884) (cited in Laidler, 2007, p. 42) had proposed this equation earlier. He also considered a more general case where $E = B + D\,T^2$, and B and D are constants. Kooij (1893) and Harcourt and Esson (1895) (cited in Laidler, 2007, p. 42) suggested equations of the forms

$$k = A\,T^m \, e^{-\frac{E}{RT}} \tag{2.130}$$

$$k = A\,T^m \tag{2.131}$$

respectively. As noted by Laidler (2007, p. 46), current practice is to use the Arrhenius equation where it is applicable. If a plot of $\ln k$ versus $1/T$ shows a significant curvature, (2.130) is the preferred choice. Transition state theory provides some justification for the use of this equation. On the other hand, there is no theoretical basis for the use of (2.131), even in cases where it fits the data well.

Theories for estimating the pre-exponential factor are discussed briefly below.

2.18.1 The collision theory

This theory was proposed by Trautz (1916) and Lewis (1918) for *gas phase* reactions. It is based on the kinetic theory of dilute gases. Consider an elementary reaction of the form

$$A_1 + A_2 \rightarrow \text{ products} \tag{2.132}$$

The reaction rate, i.e the number of molecules of A_1 consumed per unit volume per unit time is assumed to be equal to the number of collisions per unit volume per unit time between molecules of A_1 and A_2. The latter may be estimated as follows.

Using the Maxwell-Boltzmann velocity distribution for each species, the mean relative velocity between molecules of A_1 and A_2 is given by (Frost and Pearson, 1961, p. 60)

$$\overline{u} = \sqrt{\frac{8\, k_b\, T}{\pi\, \mu_m}} \tag{2.133}$$

where

$$\mu_m \equiv \frac{m_1\, m_2}{m_1 + m_2} \tag{2.134}$$

is the *reduced mass* of two molecules of masses m_1 and m_2. As the molecules are assumed to be rigid spheres of diameters d_1 and d_2, the centres of molecules of A_2 must lie in the volume $\pi\, d_{12}^2\, \overline{u} \Delta t$ if a molecule of A_1 is to collide with them in a time interval Δt. Here

$$d_{12} \equiv \frac{d_1 + d_2}{2} \tag{2.135}$$

is the mean diameter for molecules of A_1 and A_2. If n_2 is the number of *molecules* of A_2 per unit volume, the number of collisions per unit time between *a molecule* of A_1 and molecules of A_2 is

$$\hat{\Gamma}_{12} = \pi\, d_{12}^2\, \overline{u}\, n_2 \tag{2.136}$$

As there are n_1 molecules of A_1 per unit volume, the number of collisions per unit volume per unit time between molecules of A_1 and A_2 is given by

$$\hat{\Gamma} = \pi\, d_{12}^2\, \overline{u}\, n_2\, n_1 \tag{2.137}$$

or, in terms of the molar concentrations c_i by

$$\hat{\Gamma} = N_a^2\, \pi\, d_{12}^2\, \overline{u}\, c_2\, c_1 \tag{2.138}$$

where $N_a = 6.022 \times 10^{23}$ molecules/mol is the Avogadro number.

Substituting for $\overline{u}$ from (2.133) and assuming that each collision results in a reaction, i.e. the conversion of one molecule of A_1 and one molecule of A_2 to products, the *molar* reaction rate is given by

$$\dot{\beta} = N_a \sqrt{\frac{8\,\pi\,k_b\,T}{\mu_m}}\,d_{12}^2\,c_2\,c_1 \tag{2.139}$$

Consider gases at normal temperature and pressure (273 K, 1 atm), with $c_1 = c_2 = p/(R\,T)$, where R is the gas constant. The reaction rate calculated using (2.139) is of the order of 10^{10} mol/m^3-s (Frost and Pearson, 1961, p. 61), which is several orders of magnitude higher than the observed rate for many reactions.

The discrepancy can be reduced significantly by assuming that only "energetic" collisions result in a chemical reaction. An energetic collision is one for which the kinetic energy associated with the relative velocity along the line of centres exceeds a threshold value or activation energy E (Frost and Pearson, 1961, p. 65). It can be shown (Frost and Pearson, 1961, pp. 65-67) that the fraction of energetic collisions is $\exp(-E/(R\,T))$, and hence (2.139) may be replaced by

$$\dot{\beta} = N_a \sqrt{\frac{8\,\pi\,k_b\,T}{\mu_m}}\,d_{12}^2\,e^{-\frac{E}{R\,T}}\,c_2\,c_1 \tag{2.140}$$

Thus the rate constant for (2.132) is given by

$$k = N_a \sqrt{\frac{8\,\pi\,k_b\,T}{\mu_m}}\,d_{12}^2\,e^{-\frac{E}{R\,T}} \tag{2.141}$$

Comparison with the Arrhenius equation (2.129) shows that the pre-exponential factor is now a weak function of the temperature T.

For a reaction of the form

$$2\,A_1 \rightarrow \text{ products} \tag{2.142}$$

$\mu = m_1/2$ and the right hand side of (2.143) must be divided by a factor of 2 to avoid counting the collisions twice. Thus the rate constant for (2.142) is given by

$$k = 2\,N_a \sqrt{\frac{\pi\,k_b\,T}{m_1}}\,d_{12}^2\,e^{-\frac{E}{R\,T}} \tag{2.143}$$

For the reaction

$$2\,\mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I_2} \tag{2.144}$$

Lewis (1918) (cited in Laidler, 2007, p. 82) found that the pre-exponential factor predicted by (2.143) was 3.5×10^{-10} $\mathrm{m^3/mol\text{-}s}$. This value agrees very well with the observed value, but the agreement is fortuitous. For many reactions, the collision theory considerably overestimates the rate constants.

Extensions to the collision theory are described in Laidler (2007, pp. 84-87).

2.18.2 Transition state theory or activated complex theory

This theory was developed by several workers, notably Pelzer and Wigner (1932), Evans and Polanyi (1935), Eyring (1935), and Wynne-Jones and Eyring (1935). Consider a reaction of the type

$$\mathrm{A} + \mathrm{BC} \rightleftharpoons \mathrm{AB} + \mathrm{C} \tag{2.145}$$

where A, B, and C are atoms. For a system containing one atom each of A, B, and C, the potential energy of interaction U_p will vary with interatomic distances, owing to the existence of attractive and repulsive forces. For ease of analysis, consider a linear or one-dimensional configuration of the atoms (Fig. 2.2). Then

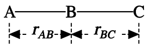

Fig. 2.2. A linear configuration of three atoms A, B, and C

$$U_p = U_p(r_{\mathrm{AB}}, r_{\mathrm{BC}}) \tag{2.146}$$

where r_{AB} is the distance between the nuclei of atoms A and B.

Equation (2.146) may be regarded as a *potential energy surface* in a space with Cartesian coordinates $(U_p, r_{\mathrm{AB}}, r_{\mathrm{BC}})$. For H atoms, the potential energy surface has been calculated using quantum mechanics. The reaction considered is

$$\mathrm{H}^{\alpha} + \mathrm{H}^{\beta} - \mathrm{H}^{\gamma} \rightarrow \mathrm{H}^{\alpha} - \mathrm{H}^{\beta} + \mathrm{H}^{\gamma} \tag{2.147}$$

where the superscripts indicate different H atoms. For a linear configuration of atoms, contours of constant U_p can be plotted in the $r(\mathrm{H}^{\alpha} - \mathrm{H}^{\beta}) - r(\mathrm{H}^{\beta} - \mathrm{H}^{\gamma})$ plane (Fig. 2.3).

The upper left hand corner of the figure represents a region where $r(\mathrm{H}^{\alpha} - \mathrm{H}^{\beta}) \gg r(\mathrm{H}^{\beta} - \mathrm{H}^{\gamma})$, and hence it corresponds to the reactants shown in (2.147). Similarly the lower right hand corner corresponds to the products shown in (2.147). The broken curve ABC is the locus of local *minima* of the potential energy U_p. It is postulated that the reaction occurs along this path of minimum energy, in the direction shown by the arrows. An examination of the numerical values of the contours intersecting this locus shows that U_p exhibits a *maximum* as the locus is traversed (Fig. 2.4). Thus the point B in Fig. 2.3 represents a *saddle point* or *col* (Laidler, 2007, p. 59).

The distance measured along ABC is called the *reaction coordinate* (Frost and Pearson, 1961, p. 81). The configuration of the atoms in the vicinity of the maximum B in Fig. 2.4 is referred to as an *activated complex* or a *transition state* (Laidler, 2007, pp. 60-61). Once the reaction coordinate and the location of the activated complex have been identified, the rate of the reaction can be calculated as discussed below. The treatment has been adapted from Laidler (2007, pp. 95-97).

The procedure consists of estimating (i) the concentration of activated complexes, and (ii) the time required for a complex to cross the transition state from left to right. The ratio of these two factors gives the reaction rate.

The reaction (2.145) is assumed to occur through an intermediate step involving the activated complex X_*:

$$\mathrm{A} + \mathrm{BC} \rightleftharpoons \mathrm{X}_* \rightarrow \mathrm{AB} + \mathrm{C} \tag{2.148}$$

In order to derive the reaction rate for the forward reaction, the key assumption is that X_* is in *equilibrium* with the reactants A and BC. This assumption is difficult to justify. For reactions whose activation energy is $\gg RT$, where R is the gas constant and T is the absolute temperature, it appears that its use may not cause large errors, unless the reactions are highly exothermic (Denbigh, 1971, p. 455). For a perfect gas mixture containing three species A, BC, X_*, it can be shown using statistical mechanics that the molar concentrations c_i are related to the *molecular* partition functions

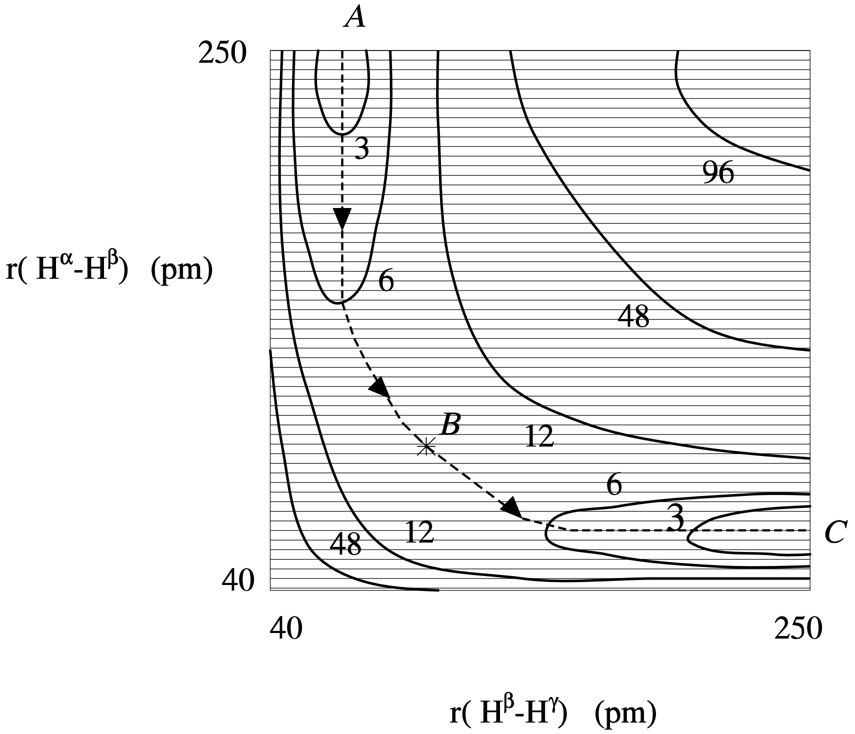

Fig. 2.3. Contours of constant potential energy U_p for a system containing three H atoms H^α, H^β, and H^γ. Here $r(H^\alpha - H^\beta)$ denotes the distance between the centres of H^α and H^β. The contours are only rough sketches, used to indicate the qualitative features. The actual contours, representing the results of Truhlar and Horowitz (1978), are given in their paper and also in Laidler (2007, p. 67). The numbers on the contours show values of U_p in kcal/mol. Adapted from Fig. 3.10 of Laidler (2007, p.67).

$\hat{q}_i$ by (McQuarrie, 2003, pp. 142-144)

$$\frac{c_{\mathrm{X}_*}}{c_{\mathrm{A}}\, c_{\mathrm{BC}}} = \frac{N_a(\hat{q}_{\mathrm{X}_*}/V)}{(\hat{q}_{\mathrm{A}}/V)\,(\hat{q}_{\mathrm{BC}}/V)}\, e^{-E_0/(RT)} \tag{2.149}$$

where $N_a = 6.022 \times 10^{23}$ molecules/mol is Avogadro's number, V is the volume of the system, and E_0 is the difference in the *molar* zero point

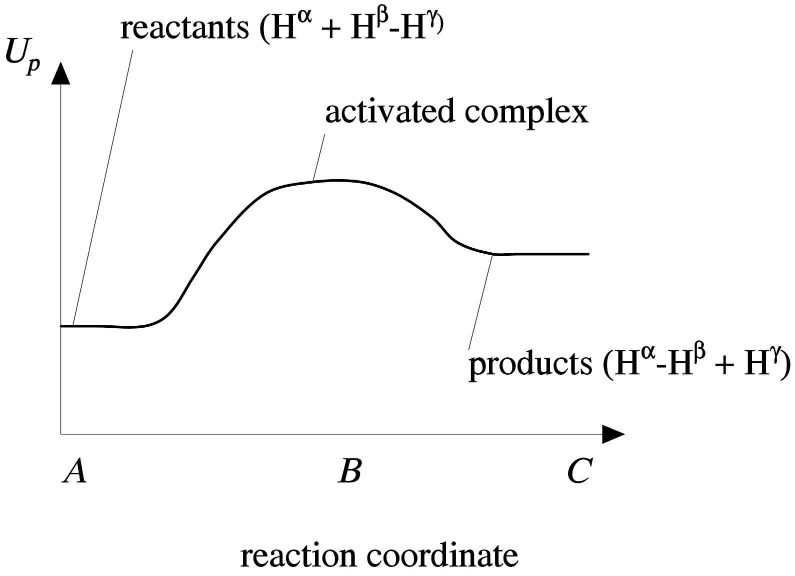

Fig. 2.4. Locus of local minima of the potential energy for the potential energy contours shown in Fig. 2.3).

energies of the activated complex and the reactants. For the first of the reactions (2.148)

$$E_0 \equiv E_{\mathrm{X}_*} - E_{\mathrm{A}} - E_{\mathrm{BC}} \tag{2.150}$$

where $E_{\mathrm{X}_*}, E_{\mathrm{A}}$ and E_{BC} are the zero point energies per mole of X_*, A, and BC, respectively, relative to an arbitrary zero of energy.

For a one-dimensional vibration of a molecule, the partition function is given by (McQuarrie, 2003, p. 96)

$$\hat{q} = \frac{1}{1 - e^{-h\,\nu/(k_b\,T)}} \tag{2.151}$$

where ν is the frequency of vibration, $h = 6.626 \times 10^{-34}$ J-s is Planck's constant, and $k_b = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant. It is assumed that the activated complex crosses the saddle point via a *very loose vibration*, i.e. the frequency $\nu \to 0$ (Laidler, 2007, p. 95). In this limit, (2.151) reduces to

$$\hat{q} = \frac{k_b\, T}{h\, \nu} \tag{2.152}$$

Thus

$$\hat{q}_{\mathrm{X}_*} = \frac{k_b\, T}{h\, \nu}\, \hat{q}'_{\mathrm{X}_*} \tag{2.153}$$

where $\hat{q}'_{\mathrm{X}_*}$ represents the partition function for all the degrees of freedom of the activated complex, except the loose vibration near the saddle point.

Equations (2.149) and (2.153) imply that

$$c_{\mathrm{X}_*} = \frac{N_a\, k_b\, T}{h\, \nu}\, \frac{(\hat{q}'_{\mathrm{X}_*}/V)}{(\hat{q}_{\mathrm{A}}/V)\,(\hat{q}_{\mathrm{BC}}/V)}\, e^{-E_0/(R\,T)}\, c_{\mathrm{A}}\, c_{\mathrm{BC}} \tag{2.154}$$

As the time required for the activated complex to cross the saddle region is $\approx 1/\nu$, the *molar* reaction rate for the forward reaction is given by

$$\dot{\beta} = \frac{c_{\mathrm{X}_*}}{1/\nu} = \frac{R\,T}{h}\, \frac{(\hat{q}'_{\mathrm{X}_*}/V)}{(\hat{q}_{\mathrm{A}}/V)\,(\hat{q}_{\mathrm{BC}}/V)}\, e^{-E_0/(R\,T)}\, c_{\mathrm{A}}\, c_{\mathrm{BC}} \tag{2.155}$$

where $R \equiv k_b\, N_a$ is the gas constant. Hence the rate constant for the forward reaction is given by

$$k = \frac{R\,T}{h}\, \frac{(\hat{q}'_{\mathrm{X}_*}/V)}{(\hat{q}_{\mathrm{A}}/V)\,(\hat{q}_{\mathrm{BC}}/V)}\, e^{-E_0/(R\,T)} \tag{2.156}$$

Note that the pre-exponential factor is now a function of the temperature, unlike in the Arrhenius equation.

2.18.3 Comparison of the theories

For the reaction

$$\mathrm{A} + \mathrm{B} \to \mathrm{AB} \tag{2.157}$$

where A and B are *atoms*, both the theories give identical expressions for the rate constant (Laidler, 2007, pp. 106-107). For reactions involving molecules, the partition functions occurring the activated complex theory involve other degrees of freedom such as rotation and vibration in addition to translation, whereas the collision theory considers only translation. As discussed in Laidler (2007, pp. 107-109), these additional degrees of freedom cause the pre-exponential factor predicted the activated complex theory to be significantly lower than than that predicted by the collision theory. Two examples are given below.

Table 2.1 compares the measured and predicted pre-exponential factors for the dimerization of cyclopentadiene (Fig. 2.5)

$$2\,C_5H_6(\text{cyclopentadiene}) \rightarrow C_{10}H_{12} \qquad (2.158)$$

and

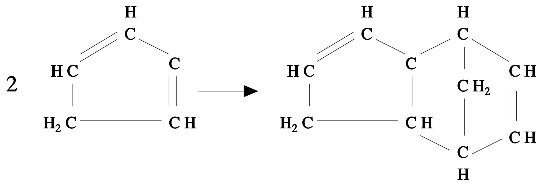

Fig. 2.5. Dimerization of cyclopentadiene.

$$2NO_2 \rightarrow 2\,NO + O_2 \qquad (2.159)$$

In both the cases, the activated complex theory gives reasonable estimates of the pre-exponential factors, whereas the collision theory overestimates them considerably.

2.18.4 Reactions in solution

Some reactions occur in both the gas phase and also in a liquid solvent. In such cases, the rate in solution is comparable to that in the gas phase (Table 2.2), except for the dimerization reaction in C_6H_6. For reactions that

Table 2.1. *Measured and predicted values of the pre-exponential factor A for the reactions (2.158) and (2.159). Source: Laidler (1965, pp. 124-125).*

	A (m^3/mol-s)	
reaction	(2.158)	(2.159)
experiment	10^4	2×10^6
collision theory	10^8	4×10^7
activated complex theory	2×10^4	2.5×10^6

occur in solution, but not in the gas phase, the solvent may significantly affect the rate (Table 2.3).

2.18.5 Catalytic reactions

A *catalyst* is a substance that increases the reaction rate without being permanently affected by the reaction. As it increases the rates of the forward and backward reactions by the same amount, the equilibrium conversion is unaffected.

As noted by Laidler (2007, p. 229), the word catalysis is derived from the Greek words *kata* (wholly) and *lyein* (loosen). The word catalyst was coined by Berzelius (1836), who studied several reactions, and is usually credited with the discovery of catalysis. However, as noted by Laidler and Cornish-Bowden (1979) (cited in Datta, 2005, p. 248-249), the phenomenon of catalysis had been discovered forty years earlier by Elizabeth Fulhame.

Catalytic reactions may be broadly classified as *homogeneous* or *heterogeneous*. In the former, the reactants, products, and catalyst are all in the same phase; in the latter, more than one phase is involved. Enzyme catalysis is usually classified under homogeneous catalysis (Laidler, 2007, p. 378).

An example of a homogeneously catalyzed gas phase reaction is provided by the decomposition of acetaldehyde in the presence of iodine (Laidler, 2007, p. 414):

$$\mathrm{CH_3CHO} \rightarrow \mathrm{CH_4} + \mathrm{CO} \tag{2.160}$$

Here I_2 acts as a catalyst, reducing the activation energy from about 200

Table 2.2. *Comparison of pre-exponential factors A and activation energies E for reactions in the gas phase and in liquids. Source: Laidler (2007, pp. 184-185).*

solvent	$\log_{10} A$ (A in m^3/mol-s)	E (kJ/mol)
(i) decomposition of N_2O_5		
gas phase	7.6	103.3
CCl_4	7.6-7.8	101.3-106.7
$CHCl_3$	7.6-7.7	102.5-102.9
(ii) dimerization of cyclopentadiene		
gas phase	0.1	69.9
CCl_4	-0.1	67.8
C_6H_6	1.1	29.7
CS_2	-0.3	74.1

kJ/mol to about 135 kJ/mol. There are many aqueous phase reactions that are catalyzed by acids and bases, such as the reaction between acetone and iodine (Laidler, 2007, p. 392).

Many industrial reactions such as the synthesis of NH_3 involve heterogeneous (solid) catalysts. Such reactions involve several steps, such as the mass transfer between the bulk fluid and the surface of the catalyst, adsorption of reactants on the surface, either surface reactions between adsorbed reactants or reactions between adsorbed and fluid-phase reactants, and desorption of reactants and products from the surface.

In the context of the transition state theory, the main effect of a solid catalyst is to lower the energy barrier (Fig. 2.6). For example, the activation energy for the decomposition of NH_3 decreases from 340 kJ/mol to 134-180 kJ/mol when a molybdenum catalyst is used (Laidler, 2007, p. 267).

Consider the unimolecular reaction A_1 (g) $\rightarrow$ A_2 (g) which is cat-

Table 2.3. *Effect on the solvent on the rate of reaction between triethylamine and ethyliodide. Here k is the second order rate constant, evaluated as 100 °. Source: Laidler (2007, p. 185).*

solvent	$10^{11}\,k$ (A in m^3/mol-s)
hexane	0.5
toluene	25.3
benzene	39.8

alyzed by a solid catalyst. Suppose it is assumed that the surface reaction is the *rate-limiting* step, i.e. of adsorption and desorption can occur at rates that are potentially much faster than the rate of surface reaction. Hence these processes may be assumed to be at *equilibrium*, and the concentrations of the adsorbed species may be calculated using the adsorption isotherms. The latter are obtained by equating the rates of adsorption and desorption of each reactant, in the absence of reactions. The above model leads to the rate expression (Schmidt, 2005, p. 303)

$$\dot{\beta} = \frac{k\,K_1\,p_1}{1 + K_1\,p_1 + K_2\,p_2} \tag{2.161}$$

where $\dot{\beta}$ is the intrinsic reaction rate, k is the rate constant, K_i and p_i are the adsorption equilibrium constants and partial pressure, respectively, of species A_i. Equation (2.163) assumes that A_2 is first formed as an adsorbed species that then desorbs, i.e. the reactions involved are

$$A_{1*} \to A_{2*} \to A_2\mathrm{g} \tag{2.162}$$

where A_{1*} represents adsorbed A_1. If A_2 (g) is formed directly from A_{1*}, we set $K_2 = 0$ in (2.163). Equation (2.163) represents an example of *Lanmuir-Hinshelwood*, or equivalently, *Hougen-Watson* kinetics, named after Langmuir (1922), Hinshelwood (1926), and Hougen and Watson (1947) (cited in Froment and Bischoff, 1990, p. 71). Instead of assuming that the surface reaction is rate-limiting, alternative assumptions may be used, leading to different rate expressions (Froment and Bischoff, 1990, pp. 76-77).

Similarly, for the reaction A_1 (g) + A_2 (g) → A_3 (g), the reaction rate is given by (Schmidt, 2005, p. 308)

$$\dot{\beta} = \frac{k\, K_1\, K_2\, p_1\, p_2}{(1 + K_1\, p_1 + K_2\, p_2 + K_3\, p_3)^2} \tag{2.163}$$

As noted by Schmidt (2005, p. 309), the use of Langmuir-Hinshelwood kinetics involves several assumptions that may not be justified in actual surface catalyzed reactions. However, it provides relatively simple kinetic models for complex heterogeneous catalytic reactions. Zhang et al. (2009) discuss the use of such models for the Fischer-Tropsch synthesis of hydrocarbons from *water gas*, which is a mixture of CO and H_2.

2.18.6 Ideal reactors

As mentioned in Chapter 1, ideal reactors are based on simple models of flow patterns and mixing in the reaction vessel.

(a) *The ideal batch reactor*

In an ideal batch reactor, the concentration and temperature fields are assumed to be *spatially uniform.* In practice, the condition can be approximately realized by vigorous agitation or stirring. In the absence of stirring, beautiful spatial patterns, caused by an interaction between diffusion and reactions, may develop in some systems (Epstein et al., 1983; Epstein and Showalter, 1996).

All the elements of the fluid spend the same amount of time in the reactor, and hence have the same *residence time.* From the viewpoint of thermodynamics, a batch reactor represents a *closed* system. The *steady states* of the batch reactor correspond to states of *reaction equilibria*, which satisfy (2.84).

Batch reactors are often used in the pharmaceutical industry, where small volumes of high-value products are made.

(b) *The ideal continuous stirred tank reactor (CSTR)*

Like in an ideal batch reactor, the concentration and temperature fields in an ideal CSTR are spatially uniform. As there are no spatial gradients, the species concentrations in the *exit* stream are identical to the corresponding values in the reactor. On the other hand, the species concentrations in the *inlet* stream are in general different from those in the reactor.

Unlike the batch reactor, the CSTR is an *open* system as it can exchange heat and mass with the surroundings. Hence it operates *away from equilibrium*, and steady states are usually *not* states of reaction equilibria.

On account of the assumption of perfect mixing, the sequence in which fluid elements leave the reactor is *uncorrelated* with the sequence in which they enter. As shown later, this leads to a *distribution of residence times* for the fluid leaving the reactor.

These reactors are widely used for polymerization reactions such as the polymerization of styrene, production of explosives, synthetic rubber, etc. Compared to tubular reactors, CSTRs are easier to clean and permit better control of the temperature.

(c) *The plug flow reactor (PFR)*

The PFR is an idealization of a tubular reactor. The velocity, temperature, and concentration fields are assumed to be *uniform* across the cross section of the reactor. In practice, this situation can be approximately realized for the case of turbulent flow through a tube with a large ratio of the length to the diameter. The latter condition ensures that axial mixing has a negligible effect on the conversion.

In a PFR, there is *perfect mixing* in the radial or transverse direction. Further, there is *no* mixing or diffusion in the axial direction. Like a CSTR, the PFR also represents an open system, and hence steady states are not states of reaction equilibrium. Owing to the assumption of plug flow, all the fluid elements have the *same* residence time. The velocity of the fluid is often treated as a constant, but this assumption must be relaxed when the density of the fluid changes significantly along the length of the tube.

The steady state equations for a PFR are similar in form to the dynamic equations for an ideal batch reactor. In many cases, the results for the latter can be translated into results for a PFR operating at a steady state.

Tubular reactors are used for many gas phase and liquid phase reactions, such as the oxidation of NO and the synthesis of NH_3. These reactors are often modelled as PFRs, but more detailed models involving complications such as radial gradients, may be required in some cases.

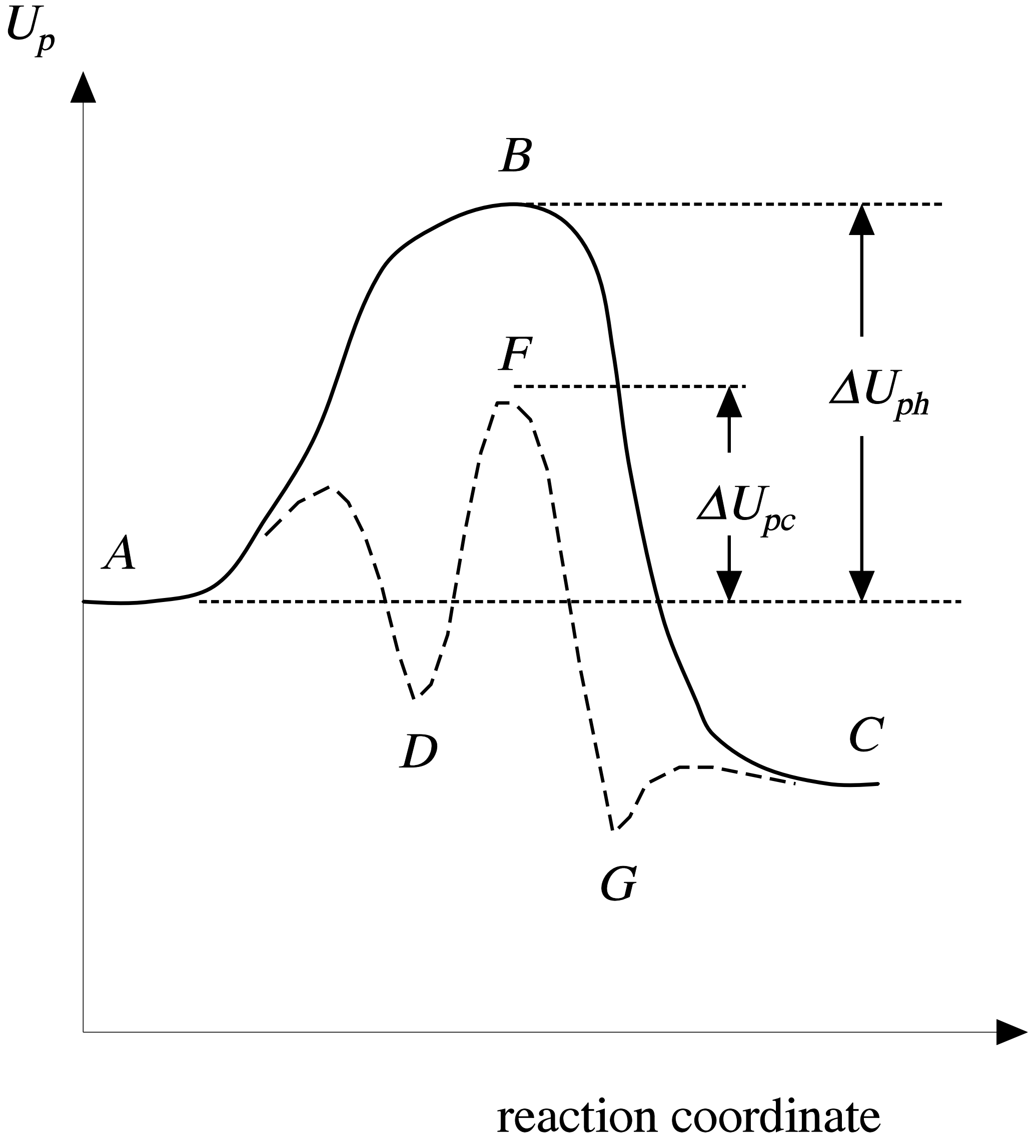

Fig. 2.6. Variation of the potential energy U_p along the reaction coordinate for an uncatalyzed gas phase reaction (—) and a solid catalyzed heterogeneous reaction (- - -). Here A, C, D, and G denote the gaseous reactants, gaseous products, adsorbed reactants, and adsorbed products, respectively. and D and F denote the activated complexes for the gas phase and heterogeneous reactions, respectively. The quantities ΔU_{ph} and ΔU_{pc} represent the energy barriers for the homogeneous and catalytic reactions, respectively. Adapted from Laidler (2007, p. 268).

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