

Chapter 4

Heat Effects

Heat transfer is one of the most common operations in the chemical industry. Consider, for example, the manufacture of ethylene glycol (an antifreeze agent) by the oxidation of ethylene to ethylene oxide and its subsequent hydration to glycol. The catalytic oxidation reaction is most effective when carried out at temperatures near 523.15 K (250°C). The reactants, ethylene and air, are therefore heated to this temperature before they enter the reactor. To design the preheater one must know how much heat is transferred. The combustion reactions of ethylene with oxygen in the catalyst bed tend to raise the temperature. However, heat is removed from the reactor, and the temperature does not rise much above 523.15 K (250°C). Higher temperatures promote the production of CO₂, an unwanted product. Design of the reactor requires knowledge of the rate of heat transfer, and this depends on the heat effects associated with the chemical reactions. The ethylene oxide product is hydrated to glycol by absorption in water. Heat is evolved not only because of the phase change and dissolution process but also because of the hydration reaction between the dissolved ethylene oxide and water. Finally, the glycol is recovered from water by distillation, a process of vaporization and condensation, which results in the separation of a solution into its components.

All of the important heat effects are illustrated by this relatively simple chemical-manufacturing process. In contrast to *sensible* heat effects, which are characterized by temperature changes, the heat effects of chemical reaction, phase transition, and the formation and separation of solutions are determined from experimental measurements made at constant temperature. In this chapter we apply thermodynamics to the evaluation of most of the heat effects that accompany physical and chemical operations. However, the heat effects of mixing processes, which depend on the thermodynamic properties of mixtures, are treated in Chap. 12.

4.1 SENSIBLE HEAT EFFECTS

Heat transfer to a system in which there are no phase transitions, no chemical reactions, and no changes in composition causes the temperature of the system to change. Our purpose here is to develop relations between the quantity of heat transferred and the resulting temperature change.

When the system is a homogeneous substance of constant composition, the phase rule indicates that fixing the values of two intensive properties establishes its state. The molar or specific internal energy of a substance may therefore be expressed as a *function of two*

other state variables. These may be arbitrarily selected as temperature and molar or specific volume:

$$U = U(T, V)$$

Whence,

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

As a result of Eq. (2.16) this becomes:

$$dU = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

The final term may be set equal to zero in two circumstances:

- For any constant-volume process, regardless of substance.
- Whenever the internal energy is independent of volume, regardless of the process. This is exactly true for ideal gases and incompressible fluids and approximately true for low-pressure gases.

In either case,

$$dU = C_V dT$$

and

$$\Delta U = \int_{T_1}^{T_2} C_V dT \quad (4.1)$$

For a mechanically reversible constant-volume process, $Q = \Delta U$, and Eq. (2.19) may be rewritten:

$$Q = \Delta U = \int_{T_1}^{T_2} C_V dT$$

Similarly, the molar or specific enthalpy may be expressed as a function of temperature and pressure:

$$H = H(T, P)$$

Whence,

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

As a result of Eq. (2.20) this becomes:

$$dH = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

Again, two circumstances allow the final term to be set equal to zero:

- For any constant-pressure process, regardless of the substance.
- Whenever the enthalpy of the substance is independent of pressure, regardless of the process. This is exactly true for ideal gases and approximately true for low-pressure gases.

In either case,

$$dH = C_P dT$$

and

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (4.2)$$

Moreover, $Q = \Delta H$ for mechanically reversible, constant-pressure, closed-system processes [Eq. (2.23)] and for the transfer of heat in steady-flow exchangers where AE_P and AE_K are negligible and $W_s = 0$. In either case,

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT \quad (4.3)$$

The common engineering application of this equation is to steady-flow heat transfer.

Temperature Dependence of the Heat Capacity

Evaluation of the integral in Eq. (4.3) requires knowledge of the temperature dependence of the heat capacity. This is usually given by an empirical equation; the two simplest expressions of practical value are:

$$\frac{C_P}{R} = \alpha + \beta T + \gamma T^2 \quad \text{and} \quad \frac{C_P}{R} = a + bT + cT^{-2}$$

where α , β , and γ and a , b , and c are constants characteristic of the particular substance. With the exception of the last term, these equations are of the same form. We therefore combine them to provide a single expression:

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2} \quad (4.4)$$

where either C or D is zero, depending on the substance considered. Since the ratio C_P/R is dimensionless, the units of C_P are governed by the choice of R .

As shown in Chap. 6, for gases it is the *ideal-gas heat capacity*, rather than the actual heat capacity, that is used in the evaluation of such thermodynamic properties as the enthalpy. The reason is that thermodynamic-property evaluation is most conveniently accomplished in two steps: first, calculation of values for a hypothetical *ideal-gas state* wherein ideal-gas heat capacities are used; second, correction of the ideal-gas-state values to the real-gas values. A real gas becomes ideal in the limit as $P \rightarrow 0$; if it were to remain ideal when compressed to finite pressures, its state would remain that of an ideal gas. Gases in their ideal-gas states have properties that reflect their individuality just as do real gases. Ideal-gas heat capacities (designated by C_P^{ig} and C_V^{ig}) are therefore different for different gases; although functions of temperature, they are independent of pressure.

Ideal-gas heat capacities increase smoothly with increasing temperature toward an upper limit, which is reached when all translational, rotational, and vibrational modes of molecular motion are fully excited [see Eq. (16.18)]. The influence of temperature on C_P^{ig} for argon, nitrogen, water, and carbon dioxide is illustrated in Fig. 4.1. Temperature dependence is expressed

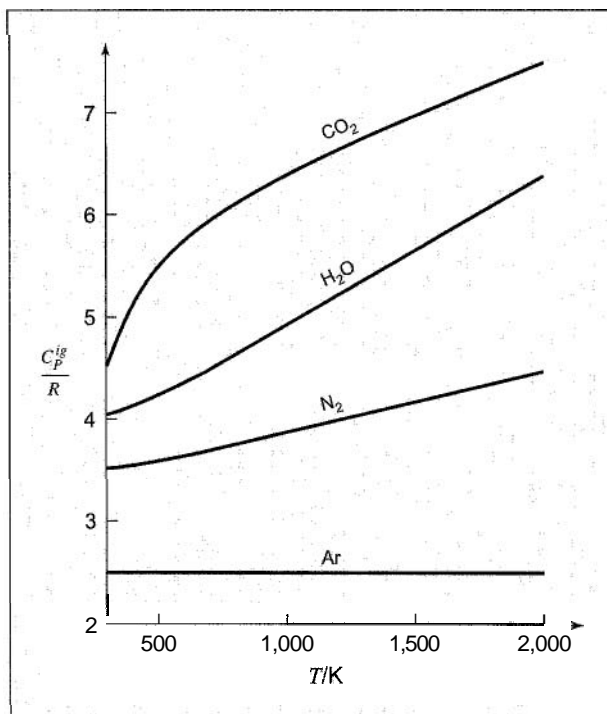


Figure 4.1 Ideal-gas heat capacities of argon, nitrogen, water, and carbon dioxide

analytically by equations such as Eq. (4.4), here written:

$$\frac{C_p^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

Values of the parameters are given in Table C.1 of App. C for a number of common organic and inorganic gases. More accurate but more complex equations are found in the literature.¹

As a result of Eq. (3.18), the two ideal-gas heat capacities are related:

$$\frac{C_V^{ig}}{R} = \frac{C_p^{ig}}{R} - 1 \quad (4.5)$$

The temperature dependence of C_V^{ig}/R follows from the temperature dependence of C_p^{ig}/R .

The effects of temperature on C_p^{ig} or C_V^{ig} are determined by experiment, most often calculated by the methods of statistical mechanics from spectroscopic data and knowledge of molecular structure. Where experimental data are not available, methods of estimation are employed, as described by Reid, Prausnitz, and Poling.²

¹See F. A. Aly and L. L. Lee, *Fluid Phase Equilibria*, vol. 6, pp. 169–179, 1981, and its bibliography; see also T. E. Daubert, R. P. Danner, H. M. Sibul, and C. C. Stebbins, *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*, Taylor & Francis, Bristol, PA, extant 1995.

²R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., chap. 6, McGraw-Hill, New York, 1987.

Although ideal-gas heat capacities are exactly correct for real gases only at zero pressure, the departure of real gases from ideality is seldom significant at pressures below several bars, and here C_P^{ig} and C_V^{ig} are usually good approximations to their heat capacities.

Example 4.1

The parameters listed in Table C.1 require use of Kelvin temperatures in Eq. (4.4). Equations of the same form may also be developed for use with temperatures in °C, (R), and (°F), but the parameter values are different. The molar heat capacity of methane in the ideal-gas state is given as a function of temperature in kelvins by:

$$\frac{C_P^{ig}}{R} = 1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2$$

where the parameter values are from Table C.1. Develop an equation for C_P^{ig}/R for temperatures in °C.

Solution 4.1

The relation between the two temperature scales is:

$$T \text{ K} = t^\circ\text{C} + 273.15$$

Therefore, as a function of t ,

$$\frac{C_P^{ig}}{R} = 1.702 + 9.081 \times 10^{-3}(t + 273.15) - 2.164 \times 10^{-6}(t + 273.15)^2$$

$$\text{or} \quad \frac{C_P^{ig}}{R} = 4.021 + 7.899 \times 10^{-3}t - 2.164 \times 10^{-6}t^2$$

Gas mixtures of constant composition may be treated in exactly the same way as pure gases. An ideal gas, by definition, is a gas whose molecules have no influence on one another. This means that each gas in a mixture exists independent of the others; its properties are unaffected by the presence of different molecules. Thus one calculates the ideal-gas heat capacity of a gas mixture as the mole-fraction-weighted sum of the heat capacities of the individual species. Consider 1 mol of gas mixture consisting of species A, B, and C, and let y_A , y_B , and y_C represent the mole fractions of these species. The molar heat capacity of the mixture in the ideal-gas state is:

$$C_{P_{\text{mixture}}}^{ig} = y_A C_{P_A}^{ig} + y_B C_{P_B}^{ig} + y_C C_{P_C}^{ig} \quad (4.6)$$

where $C_{P_A}^{ig}$, $C_{P_B}^{ig}$, and $C_{P_C}^{ig}$ are the molar heat capacities of pure A, B, and C in the ideal-gas state.

As with gases, the heat capacities of solids and liquids are found by experiment. Parameters for the temperature dependence of C_P as expressed by Eq. (4.4) are given for a few solids and liquids in Tables C.2 and C.3 of App. C. Correlations for the heat capacities of many solids and liquids are given by Perry and Green and by Daubert et al.³

Evaluation of the Sensible-Heat Integral

Evaluation of the integral $\int C_P dT$ is accomplished by substitution for C_P , followed by formal integration. For temperature limits of T_0 and T the result is conveniently expressed as follows:

$$\int_{T_0}^T \frac{C_P}{R} dT = AT_0(\tau - 1) + \frac{B}{2}T_0^2(\tau^2 - 1) + \frac{C}{3}T_0^3(\tau^3 - 1) + \frac{D}{T_0} \left(\frac{\tau - 1}{\tau} \right) \quad (4.7)$$

where
$$\tau \equiv \frac{T}{T_0}$$

Given T_0 and T , the calculation of Q or ΔH is straightforward. Less direct is the calculation of T , given T_0 and Q or ΔH . Here, an iteration scheme may be useful. Factoring $(\tau - 1)$ from each term on the right-hand side of Eq. (4.7) gives:

$$\int_{T_0}^T \frac{C_P}{R} dT = \left[AT_0 + \frac{B}{2}T_0^2(\tau + 1) + \frac{C}{3}T_0^3(\tau^2 + \tau + 1) + \frac{D}{\tau T_0} \right] (\tau - 1)$$

Since
$$\tau - 1 = \frac{T - T_0}{T_0}$$

this may be written:

$$\int_{T_0}^T \frac{C_P}{R} dT = \left[A + \frac{B}{2}T_0(\tau + 1) + \frac{C}{3}T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \right] (T - T_0)$$

We identify the quantity in square brackets as $\langle C_P \rangle_H / R$, where $\langle C_P \rangle_H$ is defined as a mean heat capacity:

$$\frac{\langle C_P \rangle_H}{R} = A + \frac{B}{2}T_0(\tau + 1) + \frac{C}{3}T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \quad (4.8)$$

Equation (4.2) may therefore be written:

$$\Delta H = \langle C_P \rangle_H (T - T_0) \quad (4.9)$$

The angular brackets enclosing C_P identify it as a mean value; subscript "H" denotes a mean value specific to enthalpy calculations, and distinguishes this mean heat capacity from a similar quantity introduced in the next chapter.

Solution of Eq. (4.9) for T gives:

$$T = \frac{\Delta H}{\langle C_P \rangle_H} + T_0 \quad (4.10)$$

³R. H. Perry and D. Green, *Perry's Chemical Engineers' Handbook*, 7th ed., Sec. 2, McGraw-Hill, New York, 1997; T. E. Daubert et al., *op. cit.*

A starting value for T (and hence for $\tau = T/T_0$) allows evaluation of $\langle C_P \rangle_H$ by Eq. (4.8). Substitution of this value into Eq. (4.10) provides a new value of T from which to reevaluate $\langle C_P \rangle_H$. Iteration continues to convergence on a final value of T .

Example 4.2

Calculate the heat required to raise the temperature of 1 mol of methane from 533.15 to 873.15 K (260 to 600 °C) in a steady-flow process at a pressure sufficiently low that methane may be considered an ideal gas.

Solution 4.2

Equation (4.3) in combination with Eq. (4.7) provides the required result. Parameters for C_P^{ig}/R come from Table C.1; temperatures are:

$$T_0 = 533.15 \text{ K} \quad T = 873.15 \text{ K} \quad \tau = \frac{873.15}{533.15} = 1.6377$$

Whence:

$$Q = \Delta H = R \int_{533.15}^{873.15} \frac{C_P^{ig}}{R} dT$$

$$Q = (8.314) \left[1.702 T_0 (\tau - 1) + \frac{9.081 \times 10^{-3}}{2} T_0^2 (\tau^2 - 1) - \frac{2.164 \times 10^{-6}}{3} T_0^3 (\tau^3 - 1) \right] = 19\,778 \text{ J}$$

Use of Defined Functions

Thermodynamic calculations often require evaluation of the integral $\int (C_P/R) dT$. This suggests that one has at hand a computer routine for computational purposes. The right-hand side of Eq. (4.7) is therefore defined as the function, $\text{ICPH}(T_0, T; A, B, C, D)$. Equation (4.7) then becomes:

$$\int_{T_0}^T \frac{C_P}{R} dT = \text{ICPH}(T_0, T; A, B, C, D)$$

The function name is ICPH , and the quantities in parentheses are the variables T_0 and T , followed by parameters A , B , C , and D . When these quantities are assigned numerical values, the notation represents a value for the integral. Thus, for the evaluation of Q in Ex. 4.2:

$$Q = 8.314 \times \text{ICPH}(533.15, 873.15; 1.702, 9.081\text{E}-3, -2.164\text{E}-6, 0.0) = 19\,778 \text{ J}$$

Representative computer programs for evaluation of the integral are given in App. D. For added flexibility the programs also evaluate the dimensionless quantity $\langle C_P \rangle_H/R$ as given

by Eq. (4.8). The right-hand side of this equation is another function, $\text{MCPH}(T_0, T; A, B, C, D)$. With this definition, Eq. (4.8) becomes:

$$\frac{\langle C_P \rangle_H}{R} = \text{MCPH}(T_0, T; A, B, C, D)$$

A specific numerical value of this function is:

$$\text{MCPH}(533.15, 873.15; 1.702, 9.081\text{E}-3, -2.164\text{E}-6, 0.0) = 6.9965$$

representing $\langle C_P \rangle_H / R$ for methane in the calculation of Ex. 4.2. By Eq. (4.9),

$$\Delta H = (8.314)(6.9965)(873.15 - 533.15) = 19\,778 \text{ J}$$

Example 4.3

What is the final temperature when heat in the amount of 422 MJ is added to 11.3 kmol of ammonia initially at 533.15 K (260°C) in a steady-flow process at approximately 1 atm?

Solution 4.3

If ΔH is the enthalpy change for 1 kmol, $Q = n \Delta H$, and

$$\Delta H = \frac{Q}{n} = \frac{422 \times 10^3}{11.3} = 37\,345 \text{ kJ kmol}^{-1}$$

With $T_0 = 533.15 \text{ K}$

we may evaluate $\langle C_P^g \rangle_H / R$ for any value of T :

$$\text{MCPH}(533.15, T; 3.578, 3.020\text{E}-3, 0.0, -0.186\text{E}+5)$$

Iteration between (A) and Eq. (4.10) starts with a value $T \geq T_0$, and converges on the final value,

$$T = 1250 \text{ K (977°C)}$$

4.2 LATENT HEATS OF PURE SUBSTANCES

When a pure substance is liquefied from the solid state or vaporized from the liquid at constant pressure, no change in temperature occurs; however, the process requires the transfer of a finite amount of heat to the substance. These heat effects are called the latent heat of fusion and the latent heat of vaporization. Similarly, there are heats of transition accompanying the change of a substance from one solid state to another; for example, the heat absorbed when rhombic crystalline sulfur changes to the monoclinic structure at 368.15 K (95°C) and 1 bar is 360 J for each g atom.

The characteristic feature of all these processes is the coexistence of two phases. According to the phase rule, a two-phase system consisting of a single species is univariant, and its intensive state is determined by the specification of just one intensive property. Thus the latent heat accompanying a phase change is a function of temperature only, and is related to other system properties by an exact thermodynamic equation:

$$\Delta H = T \Delta V \frac{dP^{\text{sat}}}{dT} \quad (4.11)$$

where for a pure species at temperature T ,

ΔH = latent heat

ΔV = volume change accompanying the phase change

P^{sat} = vapor pressure

The derivation of this equation, known as the Clapeyron equation, is given in Chap. 6.

When Eq. (4.11) is applied to the vaporization of a pure liquid, dP^{sat}/dT is the slope of the vapor pressure-vs.-temperature curve at the temperature of interest, ΔV is the difference between molar volumes of saturated vapor and saturated liquid, and ΔH is the latent heat of vaporization. Thus values of ΔH may be calculated from vapor-pressure and volumetric data.

Latent heats may also be measured calorimetrically. Experimental values are available at selected temperatures for many substances.⁴ Correlations for the latent heats of many compounds as a function of temperature are given by Daubert et al.⁵ Nevertheless, data are not always available at the temperature of interest, and in many cases the data necessary for application of Eq. (4.11) are also not known. In this event approximate methods are used for estimates of the heat effect accompanying a phase change. Since heats of vaporization are by far the most important from a practical point of view, they have received most attention. One procedure is use of a group-contribution method, known as UNIVAP.⁶ Alternative methods serve one of two purposes:

- Prediction of the heat of vaporization at the normal boiling point, i.e., at a pressure of 1 standard atmosphere, defined as 101.325 kPa.
- Estimation of the heat of vaporization at any temperature from the known value at a single temperature.

Rough estimates of latent heats of vaporization for pure liquids at their normal boiling points are given by *Trouton's rule*:

$$\frac{\Delta H_n}{RT_n} \sim 10$$

where T_n is the absolute temperature of the normal boiling point. The units of ΔH_n , R , and T_n must be chosen so that $\Delta H_n/RT_n$ is dimensionless. Dating from 1884, this rule still provides a simple check on whether values calculated by other methods are reasonable. Representative

⁴V. Majer and V. Svoboda, IUPAC Chemical Data Series No. 32, Blackwell, Oxford, 1985; R. H. Perry and D. Green, *op. cit.*, Sec. 2.

⁵T. E. Daubert et al., *op. cit.*

⁶M. Klüppel, S. Schulz, and P. Ulbig, *Fluid Phase Equilibria*, vol. 102, pp. 1–15, 1994.

experimental values for this ratio are Ar, 8.0; N₂, 8.7; O₂, 9.1; HCl, 10.4; C₆H₆, 10.5; H₂S, 10.6; and H₂O, 13.1.

Of the same nature, but not quite so simple, is the equation proposed by Riedel:⁷

$$\frac{AH_r}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}} \quad (4.12)$$

where P_c is the critical pressure in bars and T_{r_n} is the reduced temperature at T_n . Equation (4.12) is surprisingly accurate for an empirical expression; errors rarely exceed 5 percent. Applied to water it gives:

$$\frac{AH_r}{RT_n} = \frac{1.092(\ln 220.55 - 1.013)}{0.930 - 0.577} = 13.56$$

Whence, $AH_r = (13.56)(8.314)(373.15) = 42\,065 \text{ J mol}^{-1}$

This corresponds to 2334 J g^{-1} ; the steam-table value of 2257 J g^{-1} is lower by 3.4 percent.

Estimates of the latent heat of vaporization of a pure liquid at any temperature from the known value at a single temperature may be based on a known experimental value or on a value estimated by Eq. (4.12). The method proposed by Watson⁸ has found wide acceptance:

$$\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38} \quad (4.13)$$

This equation is simple and fairly accurate; its use is illustrated in the following example.

Example 4.4

Given that the latent heat of vaporization of water at 373.15 K (100°C) is 2257 kJ kg^{-1} , estimate the latent heat at 573.15 K (300°C).

Solution 4.4

$$\begin{aligned} \text{Let } \Delta H_1 &= \text{latent heat at } 373.15 \text{ K (100°C)} = 2257 \text{ kJ kg}^{-1} \\ \Delta H_2 &= \text{latent heat at } 573.15 \text{ K (300°C)} \\ T_{r_1} &= 373.15/647.1 = 0.577 \\ T_{r_2} &= 573.15/647.1 = 0.886 \end{aligned}$$

Then by Eq. (4.13),

$$\Delta H_2 = (2257) \left(\frac{1 - 0.886}{1 - 0.577} \right)^{0.38} = (2257)(0.270)^{0.38} = 1371 \text{ kJ kg}^{-1}$$

The value given in the steam tables is 1406 kJ kg^{-1} .

⁷L. Riedel, *Chem. Eng. Tech.*, vol. 26, pp. 679–683, 1954.

⁸K. M. Watson, *Ind. Eng. Chem.*, vol. 35, pp. 398–406, 1943.

4.3 STANDARD HEAT OF REACTION

Heat effects discussed so far have been for physical processes. Chemical reactions also are accompanied either by the transfer of heat or by temperature changes during the course of reaction—in some cases by both. These effects are manifestations of the differences in molecular structure, and therefore in energy, of the products and reactants. For example, the reactants in a combustion reaction possess greater energy on account of their structure than do the products, and this energy must either be transferred to the surroundings as heat or produce products at an elevated temperature.

Each of the vast number of possible chemical reactions may be carried out in many different ways, and each reaction carried out in a particular way is accompanied by a particular heat effect. Tabulation of all possible heat effects for all possible reactions is impossible. We therefore *calculate* the heat effects for reactions carried out in diverse ways from data for reactions carried out in a *standard* way. This reduces the required data to a minimum.

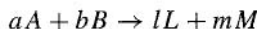
The heat associated with a specific chemical reaction depends on the temperatures of both the reactants and products. A consistent (standard) basis for treatment of reaction heat effects results when the products of reaction and the reactants are all at the *same* temperature.

Consider the flow-calorimeter method for measurement of heats of combustion of fuel gases. The fuel is mixed with air at ambient temperature and the mixture flows into a combustion chamber where reaction occurs. The combustion products enter a water-jacketed section in which they are cooled to the temperature of the reactants. Since no shaft work is produced by the process, and the calorimeter is built so that changes in potential and kinetic energy are negligible, the overall energy balance, Eq. (2.32), reduces to

$$Q = \Delta H$$

Thus the heat Q absorbed by the water is identical to the enthalpy change caused by the combustion reaction, and universal practice is to designate the enthalpy change of reaction ΔH as the *heat of reaction*.

For purposes of data tabulation with respect to the reaction,



the *standard* heat of reaction is defined as the enthalpy change when a moles of A and b moles of B in their *standard states at temperature T* react to form l moles of L and m moles of M in their *standard states at the same temperature T* .

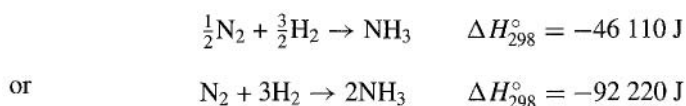
A standard state is a particular state of a species at temperature T and at specified conditions of pressure, composition, and physical condition as, e.g., gas, liquid, or solid.

A *standard-state pressure* of 1 standard atmosphere (101.325 kPa) was in use for many years, and older data tabulations are for this pressure. The standard is now 1 bar (10^5 Pa), but for purposes of this chapter, the difference is of negligible consequence. With respect to composition, the standard states used in this chapter are states of the *pure* species. For gases, the physical state is the ideal-gas state and for liquids and solids, the real state at the standard-state pressure and at the system temperature. In summary, the standard states used in this chapter are:

- *Gases*: The pure substance in the ideal-gas state at 1 bar.
- *Liquids and solids*: The real pure liquid or solid at 1 bar.

Property values in the standard state are denoted by the degree symbol. For example, C_P° is the standard-state heat capacity. Since the standard state for gases is the ideal-gas state, C_P° for gases is identical with C_P^{ig} , and the data of Table C.1 apply to the standard state for gases. All conditions for a standard state are fixed except temperature, which is always the temperature of the system. Standard-state properties are therefore functions of temperature only. The standard state chosen for gases is a hypothetical one, for at 1 bar actual gases are not ideal. However, they seldom deviate much from ideality, and in most instances enthalpies for the real-gas state at 1 bar and the ideal-gas state are little different.

When a heat of reaction is given for a particular reaction, it applies for the stoichiometric coefficients as written. If each stoichiometric coefficient is doubled, the heat of reaction is doubled. For example, the ammonia synthesis reaction may be written:



The symbol ΔH_{298}° indicates that the heat of reaction is the *standard* value for a temperature of 298.15 K (25°C).

4.4 STANDARD HEAT OF FORMATION

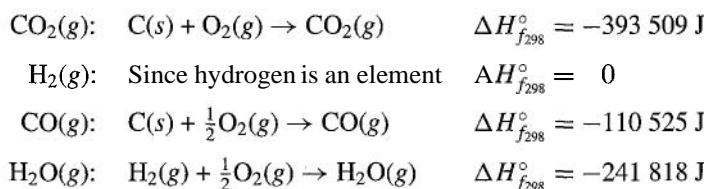
Tabulation of data for just the *standard* heats of reaction for all of the vast number of possible reactions is impractical. Fortunately, the standard heat of any reaction can be calculated if the *standard heats of formation* of the compounds taking part in the reaction are known. A *formation* reaction is defined as a reaction which forms a single compound *from its constituent elements*. For example, the reaction $\text{C} + \frac{1}{2}\text{O}_2 + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$ is the formation reaction for methanol. The reaction $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ is *not* a formation reaction, because it forms sulfuric acid not from the elements but from other compounds. Formation reactions are understood to result in the formation of 1 mol of the compound; the heat of formation is therefore based on 1 *mol of the compound formed*.

Heats of reaction at any temperature can be calculated from heat-capacity data if the value for one temperature is known; the tabulation of data can therefore be reduced to the compilation of *standard heats of formation at a single temperature*. The usual choice for this temperature is 298.15 K or 25°C. The standard heat of formation of a compound at this temperature is represented by the symbol $\Delta H_{f,298}^\circ$. The degree symbol indicates that it is the standard value, subscript *f* shows that it is a heat of formation, and the 298 is the approximate absolute temperature in kelvins. Tables of these values for common substances may be found in standard handbooks, but the most extensive compilations available are in specialized reference works.⁹ An abridged list of values is given in Table C.4 of App. C.

⁹For example, see *TRC Thermodynamic Tables—Hydrocarbons* and *TRC Thermodynamic Tables—Non-hydrocarbons*, serial publications of the Thermodynamics Research Center, Texas A & M Univ. System, College Station, Texas; "The NBS Tables of Chemical Thermodynamic Properties," *J. Physical and Chemical Reference Data*, vol. 11, supp. 2, 1982. See also, T. E. Daubert et al., *op. cit.* Where data are unavailable, estimates based only on molecular structure may be found by the methods of L. Constantinou and R. Gani, *Fluid Phase Equilibria*, vol. 103, pp. 11–22, 1995.

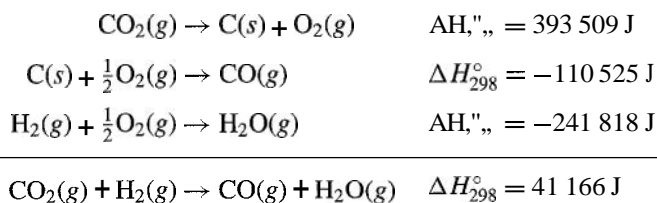
When chemical equations are combined by addition, the standard heats of reaction may also be added to give the standard heat of the resulting reaction. This is possible because enthalpy is a property, and changes in it are independent of path. In particular, formation equations and standard heats of formation may always be combined to produce any desired equation (not itself a formation equation) and its accompanying standard heat of reaction. Equations written for this purpose often include an indication of the physical state of each reactant and product, i.e., the letter *g*, *l*, or *s* is placed in parentheses after the chemical formula to show whether it is a gas, a liquid, or a solid. This might seem unnecessary since a pure chemical species at a particular temperature and 1 bar can usually exist only in one physical state. However, fictitious states are often assumed for convenience.

Consider the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ at 298.15 K (25°C). This water-gas-shift reaction is commonly encountered in the chemical industry, though it takes place only at temperatures well above 298.15 K (25°C). However, the data used are for 298.15 K (25°C), and the initial step in any calculation of heat effects concerned with this reaction is to evaluate the standard heat of reaction at 298.15 K (25°C). The pertinent formation reactions and their heats of formation from Table C.4 are:



Since the reaction is actually carried out entirely in the gas phase at high temperature, convenience dictates that the standard states of all products and reactants at 298.15 K (25°C) be taken as the ideal-gas state at 1 bar, even though water cannot actually exist as a gas at these conditions.

Writing the formation reactions so that their sum yields the desired reaction, requires that the formation reaction for CO_2 be written in reverse; the heat of reaction is then of opposite sign to the standard heat of formation:



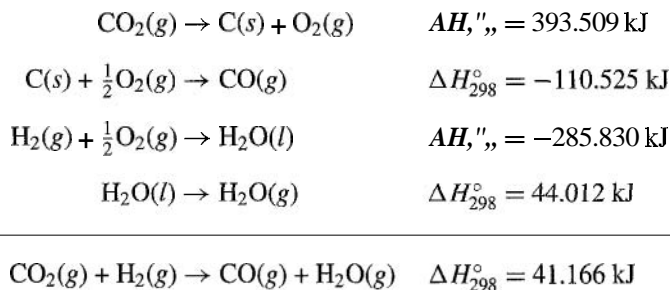
The meaning of this result is that the enthalpy of 1 mol of CO plus 1 mol of H_2O is greater than the enthalpy of 1 mol of CO_2 plus 1 mol of H_2 by 41 166 J when each product and reactant is taken as the pure gas at 298.15 K (25°C) in the ideal-gas state at 1 bar.

In this example the standard heat of formation of H_2O is available for its hypothetical standard state as a gas at 298.15 K (25°C). One might expect the value of the heat of formation of water to be listed for its actual state as a liquid at 1 bar and 298.15 K (25°C). As a matter of fact, values for both states are given in Table C.4 because they are both frequently used. This is true for many compounds that normally exist as liquids at 298.15 K (25°C) and the standard-state pressure. Cases do arise, however, in which a value is given only for the standard

state as a liquid or as an ideal gas when what is needed is the other value. Suppose that this were the case for the preceding example and that only the standard heat of formation of liquid H_2O is known. We must now include an equation for the physical change that transforms water from its standard state as a liquid into its standard state as a gas. The enthalpy change for this physical process is the difference between the heats of formation of water in its two standard states:

$$-241.818 - (-285.830) = 44.012 \text{ kJ}$$

This is approximately the latent heat of vaporization of water at 298.15 K (25°C). The sequence of steps is now:



This result is of course in agreement with the original answer.

Example 4.5

Calculate the standard heat at 298.15 K (25°C) for the following reaction:

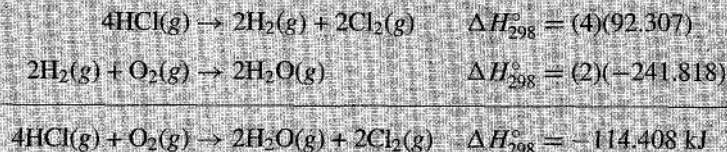


Solution 4.5

Standard heats of formation at 298.15 K (25°C) from Table C.4 are:



The following combination gives the desired result:

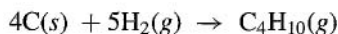


4.5 STANDARD HEAT OF COMBUSTION

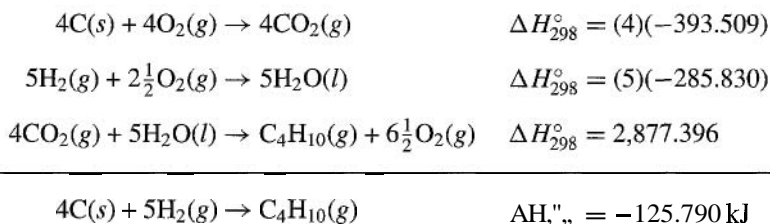
Only a few *formation* reactions can actually be carried out, and therefore data for these reactions must usually be determined indirectly. One kind of reaction that readily lends itself to experiment is the combustion reaction, and many standard heats of formation come from standard.

heats of combustion, measured calorimetrically. A combustion reaction is defined as a reaction between an element or compound and oxygen to form specified combustion products. For organic compounds made up of carbon, hydrogen, and oxygen only, the products are carbon dioxide and water, but the state of the water may be either vapor or liquid. Data are always based on 1 mol of the substance burned.

A reaction such as the formation of n-butane:



cannot be carried out in practice. However, this equation results from combination of the following combustion reactions:

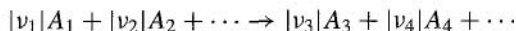


This is the value of the standard heat of formation of n-butane listed in Table C.4.

4.6 TEMPERATURE DEPENDENCE OF ΔH°

In the foregoing sections, standard heats of reaction are discussed for a reference temperature of 298.15 K (25°C). In this section we treat the calculation of standard heats of reaction at other temperatures from knowledge of the value at the reference temperature.

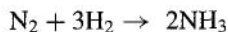
The general chemical reaction may be written:



where $|\nu_i|$ is a stoichiometric coefficient and A_i stands for a chemical formula. The species on the left are reactants; those on the right, products. The sign convention for ν_i is as follows:

positive (+) for products and negative (−) for reactants

The ν_i with their accompanying signs are called stoichiometric numbers. For example, when the ammonia synthesis reaction is written:



then $\nu_{\text{N}_2} = -1 \quad \nu_{\text{H}_2} = -3 \quad \nu_{\text{NH}_3} = 2$

This sign convention allows the definition of a standard heat of reaction to be expressed mathematically by the equation:

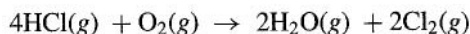
$$\Delta H^\circ \equiv \sum_i \nu_i H_i^\circ \quad (4.14)$$

where H_i° is the enthalpy of species i in its standard state and the summation is over all products and reactants. The standard-state enthalpy of a chemical compound is equal to its heat of formation plus the standard-state enthalpies of its constituent elements. If the standard-state

enthalpies of all elements are arbitrarily set equal to zero as the basis of calculation, then the standard-state enthalpy of each compound is its heat of formation. In this event, $H_i^\circ = \Delta H_{f,i}^\circ$ and Eq. (4.14) becomes:

$$\Delta H^\circ = \sum_i \nu_i \Delta H_{f,i}^\circ \quad (4.15)$$

where the summation is over all products and reactants. This formalizes the procedure described in the preceding section for calculation of standard heats of other reactions from standard heats of formation. Applied to the reaction,



Eq. (4.15) is written:

$$\Delta H^\circ = 2\Delta H_{f,\text{H}_2\text{O}}^\circ - 4\Delta H_{f,\text{HCl}}^\circ$$

With data from Table C.4 for 298.15 K, this becomes:

$$\Delta H_{298}^\circ = (2)(-241\,818) - (4)(-92\,307) = -114\,408 \text{ J or } -114.408 \text{ kJ}$$

in agreement with the result of Ex. 4.5.

For standard reactions, products and reactants are always at the standard-state pressure of 1 bar. Standard-state enthalpies are therefore functions of temperature only, and by Eq. (2.21),

$$dH_i^\circ = C_{P,i}^\circ dT$$

where subscript i identifies a particular product or reactant. Multiplying by ν_i and summing over all products and reactants gives:

$$\sum \nu_i dH_i^\circ = \sum \nu_i C_{P,i}^\circ dT$$

Since ν_i is a constant, it may be placed inside the differential:

$$\sum_i d(\nu_i H_i^\circ) = d \sum_i \nu_i H_i^\circ = \sum_i \nu_i C_{P,i}^\circ dT$$

The term $\sum_i \nu_i H_i^\circ$ is the standard heat of reaction, defined by Eq. (4.14) as ΔH° . The standard heat-capacity change of reaction is defined similarly:

$$\Delta C_P^\circ \equiv \sum_i \nu_i C_{P,i}^\circ \quad (4.16)$$

As a result of these definitions, the preceding equation becomes:

$$\boxed{d \Delta H^\circ = \Delta C_P^\circ dT} \quad (4.17)$$

This is the fundamental equation relating heats of reaction to temperature. Integration gives:

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT \quad (4.18)$$

where ΔH° and ΔH_0° are heats of reaction at temperature T and at reference temperature T_0 respectively. If the temperature dependence of the heat capacity of each product and reactant

is given by Eq. (4.4), then the integral is given by the analog of Eq. (4.7) ($\tau \equiv T/T_0$):

$$\int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT = (\Delta A)T_0(\tau - 1) + \frac{\Delta B}{2}T_0^2(\tau^2 - 1) + \frac{\Delta C}{3}T_0^3(\tau^3 - 1) + \frac{\Delta D}{T_0} \left(\frac{\tau - 1}{\tau} \right) \quad (4.19)$$

where by definition,

$$AA \equiv \sum_i \nu_i A_i$$

with analogous definitions for AB , AC , and AD .

An alternative formulation results when a mean heat capacity change of reaction is defined in analogy to Eq. (4.8):

$$\frac{\langle \Delta C_P^\circ \rangle_H}{R} = \Delta A + \frac{\Delta B}{2}T_0(\tau + 1) + \frac{\Delta C}{3}T_0^2(\tau^2 + \tau + 1) + \frac{\Delta D}{\tau T_0^2} \quad (4.20)$$

Equation (4.18) then becomes:

$$\Delta H^\circ = \Delta H_0^\circ + \langle \Delta C_P^\circ \rangle_H (T - T_0) \quad (4.21)$$

The right side of Eq. (4.19) provides a function for evaluation of the integral of interest here that is of exactly the same form as given by Eq. (4.7). The one comes from the other by simple replacement of C_P by ΔC_P° and of A , etc. by AA , etc. The same computer program therefore serves for evaluation of either integral. The only difference is in the function name:

$$\int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT = \text{IDCPH}(T_0, T; DA, DB, DC, DD)$$

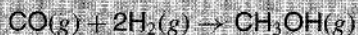
where "D" denotes "A".

Just as function MCPH is defined to represent $\langle C_P \rangle_H / R$, so function MDCPH by analogy is defined to represent $\langle \Delta C_P^\circ \rangle_H / R$; thus,

$$\frac{\langle \Delta C_P^\circ \rangle_H}{R} = \text{MDCPH}(T_0, T; DA, DB, DC, DD)$$

Example 4.6

Calculate the standard heat of the methanol-synthesis reaction at 1073.15 K (800°C):



Solution 4.6

We apply Eq. (4.15) to this reaction for reference temperature $T_0 = 298.15$ K and with heat-of-formation data from Table C.4:

$$\Delta H_O^\circ = \Delta H_{298}^\circ = -200.660 - (-110.525) = -90.135 \text{ kJ mol}^{-1}$$

Evaluation of the parameters in Eq. (4.19) is based on the following data, taken from Table C.1:

i	ν_i	A	$10^3 B$	$10^6 C$	$10^{-5} D$
CH ₃ OH	1	2.211	12.216	-3.450	0.000
CO	-1	3.376	0.557	0.000	-0.031
H ₂	-2	3.249	0.422	0.000	0.083

By definition,

$$\Delta A = (1)(2.211) + (-1)(3.376) + (-2)(3.249) = -7.663$$

$$\begin{aligned}\text{Similarly, } \Delta B &= 10.815 \times 10^{-3} \\ \Delta C &= -3.450 \times 10^{-6} \\ \Delta D &= -0.135 \times 10^5\end{aligned}$$

Thus the value of the integral of Eq. (4.25) for $T = 1073.15$ K is represented by

$$\text{IDCPH}(298.15, 1073.15; -7.663, 10.815\text{E}-3, -3.450\text{E}-6, -0.135\text{E}+5) = -1615.5 \text{ K}$$

Then by Eq. (4.18),

$$\Delta H^\circ = -90.135 + 8.314[(-1615.5)/(10^3)] = -103.566 \text{ kJ}$$

4.7 HEAT EFFECTS OF INDUSTRIAL REACTIONS

The preceding sections have dealt with the *standard* heat of reaction. Industrial reactions are rarely carried out under standard-state conditions. Furthermore, in actual reactions the reactants may not be present in stoichiometric proportions, the reaction may not go to completion, and the final temperature may differ from the initial temperature. Moreover, inert species may be present, and several reactions may occur simultaneously. Nevertheless, calculations of the heat effects of actual reactions are based on the principles already considered and are best illustrated by example.

Example 4.7

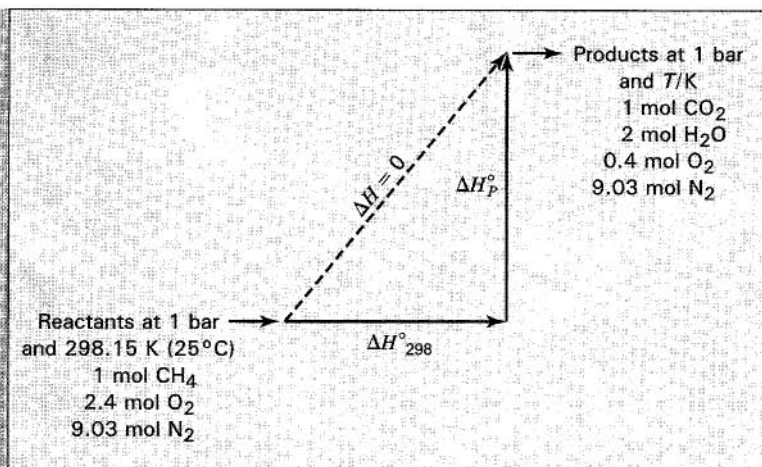
What is the maximum temperature that can be reached by the combustion of methane with 20% excess air? Both the methane and the air enter the burner at 298.15 K (25°C).

Solution 4.7

The reaction is $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}(g)$ for which,

$$\Delta H_{298}^\circ = -393\,509 + (2)(-241\,818) - (-74\,520) = -802\,625 \text{ J}$$

Since the maximum attainable temperature (called the *theoretical flame temperature*) is sought, assume that the combustion reaction goes to completion adiabatically ($Q = 0$). If the kinetic- and potential-energy changes are negligible and if $W_s = 0$, the overall energy balance for the process reduces to $\Delta H = 0$. For purposes of calculation of the final temperature, any convenient path between the initial and final states may be used. The path chosen is indicated in the diagram.



When one mole of methane burned is the basis for all calculations, the following quantities of oxygen and nitrogen are supplied by the entering air:

$$\text{Moles O}_2 \text{ required} = 2.0$$

$$\text{Moles excess O}_2 = (0.2)(2.0) = 0.4$$

$$\text{Moles N}_2 \text{ entering} = (2.4)(79/21) = 9.03$$

The gases leaving the burner contain 1 mol CO₂, 2 mol H₂O(g), 0.4 mol O₂, and 9.03 mol N₂. Since the enthalpy change must be independent of path,

$$\Delta H_{298} + \Delta H_p^\circ = \Delta H = 0 \quad (A)$$

where all enthalpies are on the basis of 1 mol CH₄ burned. The enthalpy change of the products as they are heated from 298.15 K (25°C) to T is:

$$\Delta H_p^\circ = \langle C_p^\circ \rangle_H (T - 298.15) \quad (B)$$

where we define $\langle C_p^\circ \rangle_H$ as the mean heat capacity for the *total* product stream:

$$\langle C_p^\circ \rangle_H = \sum_i n_i \langle C_{p_i}^\circ \rangle_H$$

The simplest procedure here is to sum the mean-heat-capacity equations for the products, each multiplied by its appropriate mole number. Since $C = 0$ for each product gas (Table C.1), Eq. (4.8) yields:

$$\langle C_p^\circ \rangle_H = \sum_i n_i \langle C_{p_i}^\circ \rangle_H = R \left[\sum_i n_i A_i + \frac{\sum_i n_i B_i}{2} T_0 (\tau + 1) + \frac{\sum_i n_i D_i}{\tau T_0^2} \right]$$

Data from Table C.1 are combined as follows:

$$A = \sum_i n_i A_i = (1)(5.457) + (2)(3.470) + (0.4)(3.639) + (9.03)(3.280) = 43.471$$

$$\text{Similarly, } B = \sum_i n_i B_i = 9.502 \times 10^{-3} \text{ and } D = \sum_i n_i D_i = -0.645 \times 10^5$$

For the product stream $\langle C_p^\circ \rangle_H / R$ is therefore represented by:

$$\text{MCPH}(298.15, T; 43.471, 9.502\text{E}-3, 0.0, -0.645\text{E}-5)$$

Equations (A) and (B) may be combined and solved for T :

$$T = 298.15 - \frac{\Delta H_{298}^\circ}{\langle C_p^\circ \rangle_H}$$

Because the mean heat capacities depend on T , first evaluate $\langle C_p^\circ \rangle_H$ for an assumed value of $T > 298.15$, and substitute the result in the preceding equation. This yields a new value of T for which $\langle C_p^\circ \rangle_H$ is reevaluated. The procedure continues to convergence on the final value,

$$T = 2066 \text{ K} \quad \text{or} \quad \sim 1793^\circ \text{C}$$

Example 4.8

One method for the manufacture of "synthesis gas" (primarily a mixture of CO and H_2) is the catalytic reforming of CH_4 with steam at high temperature and atmospheric pressure:



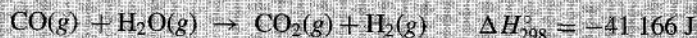
The only other reaction which occurs to an appreciable extent is the water-gas-shift reaction:



If the reactants are supplied in the ratio, 2 mol steam to 1 mol CH_4 , and if heat is supplied to the reactor so that the products reach a temperature of 1300 K, the CH_4 is completely converted and the product stream contains 17.4 mol-% CO. Assuming the reactants to be preheated to 600 K, calculate the heat requirement for the reactor.

Solution 4.8

The standard heats of reaction at 298.15 K (25°C) for the two reactions are calculated from the data of Table C.4:



These two reactions may be added to give a third reaction:



Any pair of the three reactions constitutes an independent set. The third reaction is not independent, since it is obtained by combination of the other two. The reactions most convenient to work with here are:



First determine the fraction of CH_4 converted by each of these reactions. As a basis for calculations, let 1 mol CH_4 and 2 mol steam be fed to the reactor. If x mol CH_4 reacts by Eq. (A), then $1 - x$ mol reacts by Eq. (B). On this basis the products of the reaction are:

$$\begin{array}{ll} \text{CO:} & x \\ \text{H}_2: & 3x + 4(1 - x) = 4 - x \\ \text{CO}_2: & 1 - x \\ \text{H}_2\text{O:} & 2 - x - 2(1 - x) = x \end{array}$$

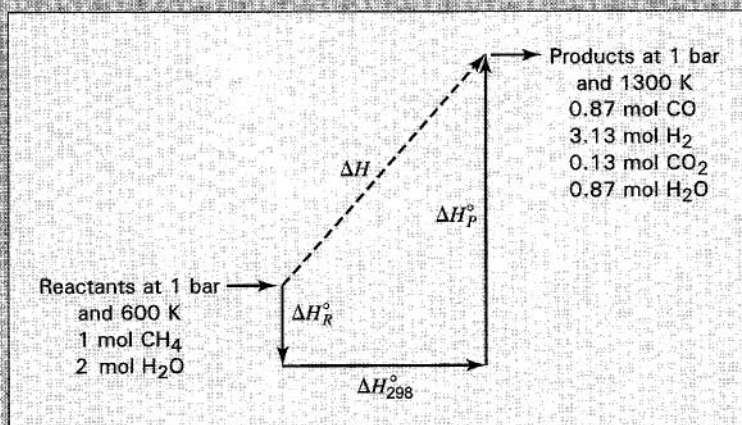
$$\text{Total: } 5 \text{ mol products}$$

The mole fraction of CO in the product stream is $x/5 = 0.174$; whence $x = 0.870$. Thus, on the basis chosen, 0.870 mol CH_4 reacts by Eq. (A) and 0.130 mol reacts by Eq. (B). Furthermore, the amounts of the species in the product stream are:

$$\begin{array}{ll} \text{Moles CO} & = x = 0.87 \\ \text{Moles H}_2 & = 4 - x = 3.13 \\ \text{Moles CO}_2 & = 1 - x = 0.13 \\ \text{Moles H}_2\text{O} & = x = 0.87 \end{array}$$

We now devise a path, for purposes of calculation, to proceed from reactants at 600 K to products at 1300 K. Since data are available for the standard heats of reaction at 298.15 K (25°C), the most convenient path is the one which includes the reactions at 298.15 K (25°C). This is shown schematically in the accompanying diagram. The dashed line represents the actual path for which the enthalpy change is ΔH . Since this enthalpy change is independent of path,

$$\Delta H = \Delta H_R^\circ + \Delta H_{298}^\circ + \Delta H_P^\circ$$



For the calculation of ΔH_{298}° , reactions (A) and (B) must both be taken into account. Since 0.87 mol CH_4 reacts by (A) and 0.13 mol reacts by (B),

$$\Delta H_{298}^\circ = (0.87)(205\,813) + (0.13)(164\,647) = 200\,460 \text{ J}$$

The enthalpy change of the reactants for cooling from 600 K to 298.15 K is:

$$\Delta H_R^\circ = \left(\sum_i n_i (C_{p,i}^\circ)_H \right) (298.15 - 600)$$

where the values of $(C_{p,i}^\circ)_H/R$ are:

$$\text{CH}_4: \text{MCPH}(298.15, 600; 1.702, 9.081\text{E}-3, -2.164\text{E}-6, 0.0) = 5.3272$$

$$\text{H}_2\text{O}: \text{MCPH}(298.15, 600; 3.470, 1.450\text{E}-3, 0.0, 0.121\text{E}+5) = 4.1888$$

Whence,

$$\begin{aligned} \Delta H_R^\circ &= (8.314)[(1)(5.3272) + (2)(4.1888)](298.15 - 600) \\ &= -34\,390 \text{ J} \end{aligned}$$

The enthalpy change of the products as they are heated from 298.15 to 1300 K is calculated similarly:

$$\Delta H_P^\circ = \left(\sum_i n_i (C_{p,i}^\circ)_H \right) (1300 - 298.15)$$

where $(C_{p,i}^\circ)_H/R$ values are:

$$\text{CO}: \text{MCPH}(298.15, 1300; 3.376, 0.557\text{E}-3, 0.0, -0.031\text{E}+5) = 3.8131$$

$$\text{H}_2: \text{MCPH}(298.15, 1300; 3.249, 0.422\text{E}-3, 0.0, 0.083\text{E}+5) = 3.6076$$

$$\text{CO}_2: \text{MCPH}(298.15, 1300; 5.457, 1.045\text{E}-3, 0.0, -1.157\text{E}+5) = 5.9935$$

$$\text{H}_2\text{O}: \text{MCPH}(298.15, 1300; 3.470, 1.450\text{E}-3, 0.0, 0.121\text{E}+5) = 4.6599$$

Whence,

$$\begin{aligned} \Delta H_P^\circ &= (8.314)[(0.87)(3.8131) + (3.13)(3.6076) \\ &\quad + (0.13)(5.9935) + (0.87)(4.6599)] \times (1300 - 298.15) \\ &= 161\,940 \text{ J} \end{aligned}$$

Therefore,

$$\begin{aligned} \Delta H &= -34\,390 + 200\,460 + 161\,940 \\ &= 328\,010 \text{ J} \end{aligned}$$

The process is one of steady flow for which W_s , Δz , and $\Delta u^2/2$ are presumed negligible. Thus,

$$Q = \Delta H = 328\,010 \text{ J}$$

This result is on the basis of 1 mol CH_4 fed to the reactor.

Example 4.9

A boiler is fired with a high-grade fuel oil (consisting only of hydrocarbons) having a standard heat of combustion (i.e. higher heating value) of $-43\,515 \text{ J g}^{-1}$ at 298.15 K (25°C) with $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ as products. The temperature of the fuel and air entering the combustion chamber is 298.15 K (25°C). The air is assumed dry. The flue gases leave at 573.15 K (300°C), and their average analysis (on a dry basis) is 11.2% CO_2 ,

0.4% CO, 6.2% O₂, and 82.2% N₂. Calculate the fraction of the heat of combustion of the oil that is transferred as heat to the boiler.

Solution 4.9

Take as a basis 100 mol dry flue gases, consisting of:

CO ₂	11.2 mol
CO	0.4 mol
O ₂	6.2 mol
N ₂	82.2 mol
<hr/>	
Total	100.0 mol

This analysis, on a dry basis, does not take into account the H₂O vapor present in the flue gases. The amount of H₂O formed by the combustion reaction is found from an oxygen balance. The O₂ supplied in the air represents 21 mol-% of the air stream. The remaining 79% is N₂, which goes through the combustion process unchanged. Thus the 82.2 mol N₂ appearing in 100 mol dry flue gases is supplied with the air, and the O₂ accompanying this N₂ is:

$$\text{Moles O}_2 \text{ entering in air} = (82.2)(21/79) = 21.85$$

However,

$$\text{Moles O}_2 \text{ in the dry flue gases} = 11.2 + 0.4/2 + 6.2 = 17.60$$

The difference between these figures is the moles of O₂ that react to form H₂O. Therefore on the basis of 100 mol dry flue gases,

$$\text{Moles H}_2\text{O formed} = (21.85 - 17.60)(2) = 8.50$$

$$\text{Moles H}_2 \text{ in the fuel} = \text{moles of water formed} = 8.50$$

The amount of C in the fuel is given by a carbon balance:

$$\text{Moles C in flue gases} = \text{moles C in fuel} = 11.2 + 0.4 = 11.60$$

These amounts of C and H₂ together give:

$$\text{Mass of fuel burned} = (8.50)(2) + (11.6)(12) = 156.2 \text{ g}$$

If this amount of fuel is burned completely to CO₂(g) and H₂O(l) at 298.15 K (25°C), the heat of combustion is:

$$\Delta H_{298}^\circ = (-43\,515)(156.2) = -6\,797\,040 \text{ J}$$

However, the reaction actually occurring does not represent complete combustion, and the H₂O is formed as vapor rather than as liquid. The 156.2 g of fuel, consisting of 11.6 mol of C and 8.5 mol of H₂, is represented by the empirical formula C_{11.6}H₁₇. Omit the 6.2 mol O₂ and 82.2 mol N₂ which enter and leave the reactor unchanged, and write the reaction:



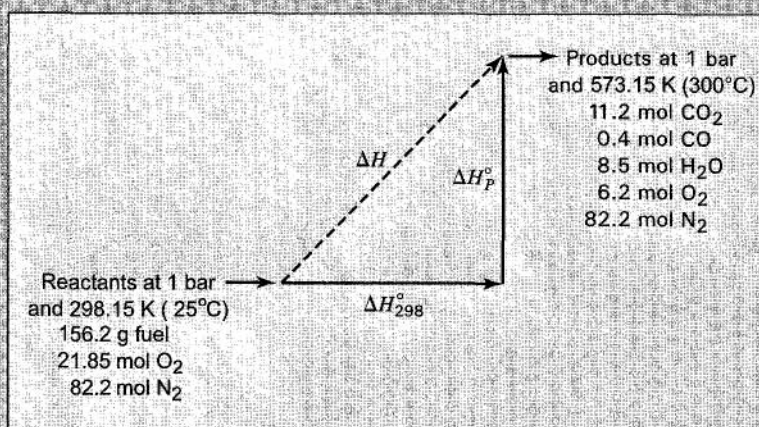
This result is obtained by addition of the following reactions, for each of which the standard heat of reaction at 298.15 K (25°C) is known:



The sum of these reactions yields the actual reaction, and the sum of the ΔH_{298}° values gives the standard heat of the reaction occurring at 298.15 K (25°C):

$$\Delta H_{298}^\circ = -6797\,040 + (44\,012)(8.5) + (282\,984)(0.4) = -6309\,740 \text{ J}$$

The actual process leading from reactants at 298.15 K (25°C) to products at 573.15 K (300°C) is represented by the dashed line in the accompanying diagram. For purposes of calculating ΔH for this process, we may use any convenient path. The one drawn with solid lines is a logical one: ΔH_{298}° has already been calculated and ΔH_p° is easily evaluated.



The enthalpy change caused by heating the products of reaction from 298.15 to 573.15 K (25 to 300°C) is:

$$\Delta H_p^\circ = \left(\sum_i n_i (C_{p,i}^\circ)_H \right) (573.15 - 298.15)$$

where the $(C_{p,i}^\circ)_H/R$ values are:

$$\text{CO}_2: \text{MCPH}(298.15, 573.15; 5.457, 1.045\text{E}-3, 0.0, -1.157\text{E}+5) = 5.2352$$

$$\text{CO}: \text{MCPH}(298.15, 573.15; 3.376, 0.557\text{E}-3, 0.0, -0.031\text{E}+5) = 3.6005$$

$$\text{H}_2\text{O}: \text{MCPH}(298.15, 573.15; 3.470, 1.450\text{E}-3, 0.0, 0.121\text{E}+5) = 4.1725$$

$$\text{O}_2: \text{MCPH}(298.15, 573.15; 3.639, 0.506\text{E}-3, 0.0, -0.227\text{E}+5) = 3.7267$$

$$\text{N}_2: \text{MCPH}(298.15, 573.15; 3.280, 0.593\text{E}-3, 0.0, 0.040\text{E}+5) = 3.5618$$

Whence,

$$\begin{aligned}\Delta H_p^\circ &= (8.314)[(11.2)(5.2352) + (0.4)(3.6005) + (8.5)(4.1725) \\ &\quad + (6.2)(3.7267) + (82.2)(3.5618)](573.15 - 298.15) \\ &= 940\,660 \text{ J}\end{aligned}$$

and

$$\Delta H = \Delta H_{298}^\circ + \Delta H_p^\circ = -6309\,740 + 940\,660 = -5369\,080 \text{ J}$$

Since the process is one of steady flow for which the shaft work and kinetic- and potential-energy terms in the energy balance [Eq. (2.32)] are zero or negligible, $\Delta H = Q$. Thus, $Q = -5369.08 \text{ kJ}$, and this amount of heat is transferred to the boiler for every 100 mol dry flue gases formed. This represents

$$\frac{5369\,080}{6797\,040}(100) = 79.0\%$$

of the heat of combustion of the fuel.

In the foregoing examples of reactions that occur at approximately 1 bar, we have tacitly assumed that the heat effects of reaction are the same whether gases are mixed or pure, an acceptable procedure for low pressures. For reactions at elevated pressures, this may not be the case, and it may be necessary to account for the effects of pressure and of mixing on the heat of reaction. However, these effects are usually small.

PROBLEMS

- 4.1. For steady flow in a heat exchanger at approximately atmospheric pressure, what is the final temperature:
 - (a) When 10 mol of SO_2 is heated from 473.15 to 1373.15 K (200 to 1100°C)?
 - (b) When 12 mol of propane is heated from 523.15 to 1473.15 K (250 to 1200°C)?
- 4.2. For steady flow through a heat exchanger at approximately atmospheric pressure, what is the final temperature,
 - (a) When heat in the amount of 800 kJ is added to 10 mol of ethylene initially at 473.15 K (200°C)?
 - (b) When heat in the amount of 2500 kJ is added to 15 mol of 1-butene initially at 533.15 K (260°C)?
 - (c) When heat in the amount of 1055 GJ is added to 18.14 kmol of ethylene initially at 533.15 K (260°C)?
- 4.3. If $7.08 \text{ m}^3 \text{ s}^{-1}$ of air at 322.15 K (50°C) and approximately atmospheric pressure is preheated for a combustion process to 773.15 K (500°C), what rate of heat transfer is required?
- 4.4. How much heat is required when 10 000 kg of CaCO_3 is heated at atmospheric pressure from 323.15 to 1153.15 K (50°C to 880°C)?

- 4.5. If the heat capacity of a substance is correctly represented by an equation of the form,

$$C_P = A + BT + CT^2$$

show that the error resulting when $\langle C_P \rangle_H$ is assumed equal to C_P evaluated at the arithmetic mean of the initial and final temperatures is $C(T_2 - T_1)^2/12$.

- 4.6. If the heat capacity of a substance is correctly represented by an equation of the form,

$$C_P = A + BT + DT^{-2}$$

show that the error resulting when $\langle C_P \rangle_H$ is assumed equal to C_P evaluated at the arithmetic mean of the initial and final temperatures is:

$$\frac{D}{T_1 T_2} \left(\frac{T_2 - T_1}{T_2 + T_1} \right)^2$$

- 4.7. Calculate the heat capacity of a gas sample from the following information: The sample comes to equilibrium in a flask at 298.15 K (25°C) and 121.3 kPa. A stopcock is opened briefly, allowing the pressure to drop to 101.3 kPa. With the stopcock closed, the flask warms, returning to 298.15 K (25°C), and the pressure is measured as 104.0 kPa. Determine C_P in $\text{J mol}^{-1} \text{K}^{-1}$ assuming the gas to be ideal and the expansion of the gas remaining in the flask to be reversible and adiabatic.
- 4.8. A process stream is heated as a gas from 298.15 to 523.15 K (25°C to 250°C) at constant pressure. A quick estimate of the energy requirement is obtained from Eq. (4.3), with C_P taken as constant and equal to its value at 298.15 K (25°C). Is the estimate of Q likely to be low or high? Why?
- 4.9. Handbook values for the latent heats of vaporization in J g^{-1} are given in the table for a number of pure liquids at 298.15 K (25°C) and at T_n , the normal boiling point (App. B).

	ΔH^{lv} at 298.15 K (25°C)	ΔH^{lv} at T_n
n-Pentane	366.3	357.2
n-Hexane	366.1	336.7
Benzene	433.3	393.9
Toluene	412.3	363.2
Cyclohexane	392.5	358.2

For one of these substances, calculate:

- (a) The value of the latent heat at T_n by Eq. (4.13), given the value at 298.15 K (25°C).
 (b) The value of the latent heat at T_n by Eq. (4.12).

By what percentages do these values differ from the one listed in the table?

- 4.10. Table 9.1 lists the thermodynamic properties of saturated liquid and vapor tetrafluoroethane. Making use of the vapor pressures as a function of temperature and of the saturated-liquid and saturated-vapor volumes, calculate the latent heat of vaporization by Eq. (4.11) at one of the following temperatures and compare the result with the value calculated from the enthalpy values given in the table.
- (a) 258.15 K (−15°C), (b) 272.15 K (−1°C), (c) 286.15 K (13°C), (d) 300.15 K (27°C), (e) 313.15 K (40°C).

- 4.11.** Handbook values for the latent heats of vaporization in J g^{-1} are given in the table for several pure liquids at 273.15 K (0°C) and at T_n , the normal boiling point (App. B).

	ΔH^{lv} at 273.15 K (0°C)	ΔH^{lv} at T_n
Chloroform	270.9	246.9
Methanol	1189.5	1099.5
Tetrachloromethane	217.8	194.2

For one of these substances, calculate:

- (a) The value of the latent heat at T_n by Eq. (4.13), given the value at 273.15 K (0°C).
 (b) The value of the latent heat at T_n by Eq. (4.12).

By what percentages do these values differ from the one listed in the table?

- 4.12.** For one of the following liquids, determine the heat of vaporization at its normal boiling point by application of the Clapeyron equation to the given vapor-pressure equation. Use generalized correlations from Chap. 3 to estimate ΔV .

(a) Benzene: $\ln P^{\text{sat}}/\text{kPa} = 13.8594 - \frac{2773.78}{T/\text{K} - 53.00}$

(b) Ethylbenzene: $\ln P^{\text{sat}}/\text{kPa} = 14.0045 - \frac{3279.47}{T/\text{K} - 59.95}$

(c) n-Heptane: $\ln P^{\text{sat}}/\text{kPa} = 13.8587 - \frac{2911.32}{T/\text{K} - 56.51}$

(d) n-Pentane: $\ln P^{\text{sat}}/\text{kPa} = 13.8183 - \frac{2447.07}{T/\text{K} - 39.94}$

(e) Toluene: $\ln P^{\text{sat}}/\text{kPa} = 14.0098 - \frac{3103.01}{T/\text{K} - 53.36}$

- 4.13.** A method for determination of the second virial coefficient of a pure gas is based on the Clapeyron equation and measurements of the latent heat of vaporization ΔH^{lv} , the molar volume of saturated liquid V^l , and the vapor pressure P^{sat} . Determine B in $\text{cm}^3 \text{mol}^{-1}$ for methyl ethyl ketone at 348.15 K (75°C) from the following data at this temperature:

$$\Delta H^{lv} = 31\,600 \text{ J mol}^{-1} \quad V^l = 96.49 \text{ cm}^3 \text{mol}^{-1}$$

$$\ln P^{\text{sat}}/\text{kPa} = 48.157543 - 5622.7/T - 4.705\,04 \ln T \quad [T = \text{K}]$$

- 4.14.** One hundred kmol per hour of subcooled liquid at 300 K and 3 bar is superheated to 500 K in a steady-flow heat exchanger. Estimate the exchanger duty (in kW) for one of the following:

- (a) Methanol, for which $T^{\text{sat}} = 368.0 \text{ K}$ at 3 bar.
 (b) Benzene, for which $T^{\text{sat}} = 392.3 \text{ K}$ at 3 bar.
 (c) Toluene, for which $T^{\text{sat}} = 426.9 \text{ K}$ at 3 bar.

- 4.15.** Saturated-liquid benzene at pressure $P_1 = 10$ bar ($T_1^{\text{sat}} = 451.7$ K) is throttled in a steady-flow process to a pressure $P_2 = 1.2$ bar ($T_2^{\text{sat}} = 358.7$ K), where it is a liquid/vapor mixture. Estimate the molar fraction of the exit stream that is vapor. For liquid benzene, $C_P = 162 \text{ J mol}^{-1} \text{ K}^{-1}$. Ignore the effect of pressure on the enthalpy of liquid benzene.
- 4.16.** Estimate $\Delta H_{f,298}^\circ$ for one of the following compounds as a liquid at 298.15 K (25°C).
(a) Acetylene, (b) 1,3-Butadiene, (c) Ethylbenzene, (d) n-Hexane, (e) Styrene.
- 4.17.** A reversible compression of 1 mol of an ideal gas in a piston/cylinder device results in a pressure increase from 1 bar to P_2 and a temperature increase from 400 K to 950 K. The path followed by the gas during compression is given by

$$P V^{1.55} = \text{const}$$

and the molar heat capacity of the gas is given by

$$C_P/R = 3.85 + 0.57 \times 10^{-3} T \quad [T = \text{K}]$$

Determine the heat transferred during the process and the final pressure.

- 4.18.** Hydrocarbon fuels can be produced from methanol by reactions such as the following, which yields 1-hexene:



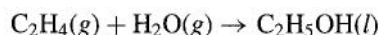
Compare the standard heat of combustion at 298.15 K (25°C) of $6\text{CH}_3\text{OH}(g)$ with the standard heat of combustion at 298.15 K (25°C) of $\text{C}_6\text{H}_{12}(g)$ for reaction products $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$.

- 4.19.** Calculate the theoretical flame temperature when ethylene at 298.15 K (25°C) is burned with:
- The theoretical amount of air at 298.15 K (25°C).
 - 25% excess air at 298.15 K (25°C).
 - 50% excess air at 298.15 K (25°C).
 - 100% excess air at 298.15 K (25°C).
 - 50% excess air preheated to 773.15 K (500°C).
- 4.20.** What is the standard heat of combustion of n-pentane gas at 298.15 K (25°C) if the combustion products are $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$?
- 4.21.** Determine the standard heat of each of the following reactions at 298.15 K (25°C):
- $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$
 - $4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$
 - $3\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(l) + \text{NO}(g)$
 - $\text{CaC}_2(s) + \text{H}_2\text{O}(l) \rightarrow \text{C}_2\text{H}_2(g) + \text{CaO}(s)$
 - $2\text{Na}(s) + 2\text{H}_2\text{O}(g) \rightarrow 2\text{NaOH}(s) + \text{H}_2(g)$
 - $6\text{NO}_2(g) + 8\text{NH}_3(g) \rightarrow 7\text{N}_2(g) + 12\text{H}_2\text{O}(g)$
 - $\text{C}_2\text{H}_4(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \langle(\text{CH}_2)_2\rangle\text{O}(g)$

- (h) $\text{C}_2\text{H}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow ((\text{CH}_2)_2)\text{O}(\text{g})$
 (i) $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g})$
 (j) $\text{CO}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g}) + \text{H}_2\text{O}(\text{g})$
 (k) $\text{CH}_3\text{OH}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{g})$
 (l) $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + 2\text{SO}_2(\text{g})$
 (m) $\text{H}_2\text{S}(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow 3\text{H}_2(\text{g}) + \text{SO}_2(\text{g})$
 (n) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
 (o) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 (p) $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{l})$
 (q) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$
 (r) $\text{CH}_3\text{CHO}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$
 (s) $\text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{COOH}(\text{l}) + \text{H}_2\text{O}(\text{l})$
 (t) $\text{C}_2\text{H}_5\text{CH:CH}_2(\text{g}) \rightarrow \text{CH}_2\text{:CHCH:CH}_2(\text{g}) + \text{H}_2(\text{g})$
 (u) $\text{C}_4\text{H}_{10}(\text{g}) \rightarrow \text{CH}_2\text{:CHCH:CH}_2(\text{g}) + 2\text{H}_2(\text{g})$
 (v) $\text{C}_2\text{H}_5\text{CH:CH}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CH}_2\text{:CHCH:CH}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
 (w) $4\text{NH}_3(\text{g}) + 6\text{NO}(\text{g}) \rightarrow 6\text{H}_2\text{O}(\text{g}) + 5\text{N}_2(\text{g})$
 (x) $\text{N}_2(\text{g}) + \text{C}_2\text{H}_2(\text{g}) \rightarrow 2\text{HCN}(\text{g})$
 (y) $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5(\text{g}) \rightarrow \text{C}_6\text{H}_5\text{CH:CH}_2(\text{g}) + \text{H}_2(\text{g})$
 (z) $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \text{CO}(\text{g})$

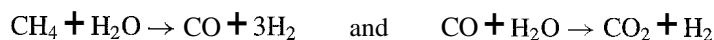
- 4.22.** Determine the standard heat for one of the reactions of Pb. 4.21: Part (a) at 873.15 K (600°C), Part (b) at 773.15 K (500°C), Part (f) at 923.15 K (650°C), Part (i) at 973.15 K (700°C), Part (j) at 583.15 K (310°C), Part (l) at 683.15 K (410°C), Part (m) at 850 K, Part (n) at 1300 K, Part (o) at 1073.15 K (800°C), Part (r) at 723.15 K (450°C), Part (t) at 733.15 K (460°C), Part (u) at 750 K, Part (v) at 900 K, Part (w) at 673.15 K (400°C), Part (x) at 648.15 K (375°C), Part (y) at 1083.15 K (810°C).
- 4.23.** Develop a general equation for the standard heat of reaction as a function of temperature for one of the reactions given in parts (a), (b), (e), (f), (g), (h), (j), (k), (l), (m), (n), (o), (r), (t), (u), (v), (w), (x), (y), and (z) of Pb. 4.21.
- 4.24.** Natural gas (assume pure methane) is delivered to a city via pipeline at a volumetric rate of 4.0 mega normal m³ per day. If the selling price of the gas is \$5.00 per GJ of higher heating value, what is the expected revenue in dollars per day? Normal conditions are 273.15 K (PC) and 1 atm.
- 4.25.** Natural gases are rarely pure methane; they usually also contain other light hydrocarbons and nitrogen. Determine an expression for the standard heat of combustion as a function of composition for a natural gas containing methane, ethane, propane, and nitrogen. Assume liquid water as a product of combustion. Which of the following natural gases has the highest heat of combustion?
- (a) $y_{\text{CH}_4} = 0.95$, $y_{\text{C}_2\text{H}_6} = 0.02$, $y_{\text{C}_3\text{H}_8} = 0.02$, $y_{\text{N}_2} = 0.01$.
 (b) $y_{\text{CH}_4} = 0.90$, $y_{\text{C}_2\text{H}_6} = 0.05$, $y_{\text{C}_3\text{H}_8} = 0.03$, $y_{\text{N}_2} = 0.02$.
 (c) $y_{\text{CH}_4} = 0.85$, $y_{\text{C}_2\text{H}_6} = 0.07$, $y_{\text{C}_3\text{H}_8} = 0.03$, $y_{\text{N}_2} = 0.05$.

- 4.26.** If the heat of combustion of urea, $(\text{NH}_2)_2\text{CO}(s)$, at 298.15 K (25°C) is $631\,660\text{ J mol}^{-1}$ when the products are $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$, and $\text{N}_2(g)$, what is $\Delta H_{f,298}^\circ$ for urea at 298.15 K (25°C)?
- 4.27.** The higher heating value (HHV) of a fuel is its standard heat of combustion at 298.15 K (25°C) with liquid water as a product; the lower heating value (LHV) is for water vapor as product.
- Explain the origins of these terms.
 - Determine the HHV and the LHV for natural gas, modeled as pure methane.
 - Determine the HHV and the LHV for a home-heating oil, modeled as pure liquid n-decane. For n-decane as a liquid $\Delta H_{f,298}^\circ = -249\,700\text{ J mol}^{-1}$.
- 4.28.** A light fuel oil with an average chemical composition of $\text{C}_{10}\text{H}_{18}$ is burned with oxygen in a bomb calorimeter. The heat evolved is measured as $43\,960\text{ J g}^{-1}$ for the reaction at 298.15 K (25°C). Calculate the standard heat of combustion of the fuel oil at 298.15 K (25°C) with $\text{H}_2\text{O}(g)$ and $\text{CO}_2(g)$ as products. Note that the reaction in the bomb occurs at constant volume, produces liquid water as a product, and goes to completion.
- 4.29.** Methane gas is burned completely with 30% excess air at approximately atmospheric pressure. Both the methane and the air enter the furnace at 303.15 K (30°C) saturated with water vapor, and the flue gases leave the furnace at 1773.15 K (1500°C). The flue gases then pass through a heat exchanger from which they emerge at 323.15 K (50°C). Per mole of methane, how much heat is lost from the furnace, and how much heat is transferred in the heat exchanger?
- 4.30.** Ammonia gas enters the reactor of a nitric acid plant mixed with 30% more dry air than is required for the complete conversion of the ammonia to nitric oxide and water vapor. If the gases enter the reactor at 348.15 K (75°C), if conversion is 80%, if no side reactions occur, and if the reactor operates adiabatically, what is the temperature of the gases leaving the reactor? Assume ideal gases.
- 4.31.** Ethylene gas and steam at 593.15 K (320°C) and atmospheric pressure are fed to a reaction process as an equimolar mixture. The process produces ethanol by the reaction:



The liquid ethanol exits the process at 298.15 K (25°C). What is the heat transfer associated with this overall process per mole of ethanol produced?

- 4.32.** A gas mixture of methane and steam at atmospheric pressure and 773.15 K (500°C) is fed to a reactor, where the following reactions occur:



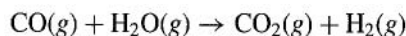
The product stream leaves the reactor at 1123.15 K (850°C). Its composition (mole fractions) is:

$$y_{\text{CO}_2} = 0.0275 \quad y_{\text{CO}} = 0.1725 \quad y_{\text{H}_2\text{O}} = 0.1725 \quad y_{\text{H}_2} = 0.6275$$

Determine the quantity of heat added to the reactor per mole of product gas.

- 4.33.** A fuel consisting of 75 mol-% methane and 25 mol-% ethane enters a furnace with 80% excess air at 303.15 K (30°C). If 800 GJ per kmol of fuel is transferred as heat to boiler tubes, at what temperature does the flue gas leave the furnace? Assume complete combustion of the fuel.
- 4.34.** The gas stream from a sulfur burner consists of 15 mol-% SO₂, 20 mol-% O₂, and 65 mol-% N₂. The gas stream at atmospheric pressure and 673.15 K (400°C) enters a catalytic converter where 86% of the SO₂ is further oxidized to SO₃. On the basis of 1 mol of gas entering, how much heat must be removed from the converter so that the product gases leave at 773.15 K (500°C)?

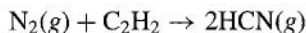
- 4.35.** Hydrogen is produced by the reaction:



The feed stream to the reactor is an equimolar mixture of carbon monoxide and steam, and it enters the reactor at 398.15 K (125°C) and atmospheric pressure. If 60% of the H₂O is converted to H₂ and if the product stream leaves the reactor at 698.15 K (425°C), how much heat must be transferred from the reactor?

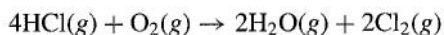
- 4.36.** A direct-fired dryer burns a fuel oil with a net heating value of 44 200 kJ kg⁻¹. [The *net* heating value is obtained when the products of combustion are CO₂(g) and H₂O(g).] The composition of the oil is 85% carbon, 12% hydrogen, 2% nitrogen, and 1% water by weight. The flue gases leave the dryer at 477.15 K (204°C), and a partial analysis shows that they contain 3 mole-% CO₂ and 11.8 mole-% CO on a dry basis. The fuel, air, and material being dried enter the dryer at 298.15 K (25°C). If the entering air is saturated with water and if 30% of the net heating value of the oil is allowed for heat losses (including the sensible heat carried out with the dried product), how much water is evaporated in the dryer per kg of oil burned?

- 4.37.** An equimolar mixture of nitrogen and acetylene enters a steady-flow reactor at 298.15 K (25°C) and atmospheric pressure. The only reaction occurring is:



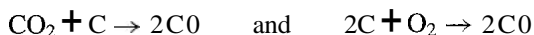
The product gases leave the reactor at 873.15 K (600°C) and contain 24.2 mole-% HCN. How much heat is supplied to the reactor per mole of product gas?

- 4.38.** Chlorine is produced by the reaction:



The feed stream to the reactor consists of 60 mol-% HCl, 36 mol-% O₂, and 4 mol-% N₂, and it enters the reactor at 823.15 K (550°C). If the conversion of HCl is 75% and if the process is isothermal, how much heat must be transferred from the reactor per mole of the entering gas mixture?

- 4.39.** A gas consisting only of CO and N₂ is made by passing a mixture of flue gas and air through a bed of incandescent coke (assume pure carbon). The two reactions that occur both go to completion:



They yield a flue gas of composition: 12.8 mol-% CO, 3.7 mol-% CO₂, 5.4 mol-% O₂, and 78.1 mol-% N₂. The flue gas/air mixture is so proportioned that the heats of the two reactions cancel, and the temperature of the coke bed is therefore constant. If this temperature is 1148.15 K (875°C), if the feed stream is preheated to 1148.15 K (875°C), and if the process is adiabatic, what ratio of moles of flue gas to moles of air is required, and what is the composition of the gas produced?

4.40. A fuel gas consisting of 94 mole-% methane and 6 mole-% nitrogen is burned with 35% excess air in a continuous water heater. Both fuel gas and air enter dry at 298.15 K (25°C). Water is heated at a rate of 34.0 kg s⁻¹ from 298.15 K (25°C) to 368.15 K (95°C). The flue gases leave the heater at 483.15 K (210°C). Of the entering methane, 70% burns to carbon dioxide and 30% burns to carbon monoxide. What volumetric flow rate of fuel gas is required if there are no heat losses to the surroundings?

4.41. A process for the production of 1,3-butadiene results from the catalytic dehydrogenation at atmospheric pressure of 1-butene according to the reaction:



To suppress side reactions, the 1-butene feed stream is diluted with steam in the ratio of 10 moles of steam per mole of 1-butene. The reaction is carried out *isothermally* at 798.15 K (525°C), and at this temperature 33% of the 1-butene is converted to 1,3-butadiene. How much heat is transferred to the reactor per mole of entering 1-butene?