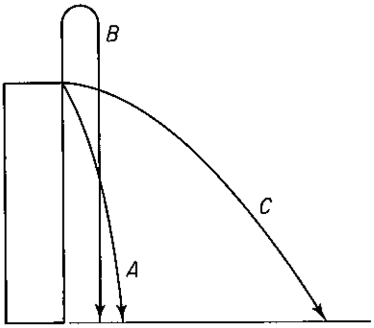
your estimate of the percentage of the coal now mined in the U.S. that would have to be added in order to fulfill this proposal? Assume 3.26 bbl of liquid per ton of coal.

3. Three baseballs are thrown from the top of a four-story building as shown in the figure. All have the same initial speed. Which of the following answers would you say best reflects the speed of the balls when they hit the ground?
   (1) A is greatest
   (2) B is greatest
   (3) C is greatest
   (4) A and C are the same and greatest
   (5) A and B are the same and greatest
   (6) All have the same speed



4.2 HEAT CAPACITY

Your objectives in studying this section are to be able to:

1. Define heat capacity.
2. Convert an expression for the heat capacity from one set of units to another.
3. Look up from a reference source an equation that expresses the heat capacity as a function of temperature, and compute the heat capacity at a given temperature.
4. Estimate the value of the heat capacity for solids and liquids.
5. Fit empirical heat capacity data with a suitable function of temperature by estimating the values of the coefficients in the function.

Before formulating the general energy balance, we shall discuss in some detail the calculation of enthalpy changes and provide some typical examples of such calculations. Our discussion will be initiated with consideration of the heat capacity C_p.

The two heat capacities have been defined as

(a) $$C_p = \left(\frac{\partial \hat{H}}{\partial T}\right)_p$$

(b)

$$C_v = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}}$$

To give these two quantities some physical meaning, you can think of them as representing the amount of energy required to increase the temperature of a substance by 1 degree, energy that might be provided by heat transfer in certain specialized processes, but can be provided by other means as well. To determine from experiments values of C_p (or C_v), the enthalpy (or internal energy) change must first be calculated from an energy balance, and then the heat capacity evaluated. We will discuss C_p as C_v is not used very often.

Suppose that you want to calculate the heat capacity of steam at 10.0 kPa (45.8°C). You can determine the enthalpy change at essentially constant pressure from the steam tables (which list experimental values) as

$$H_{47.7°C} - H_{43.8°C} = (2588.1 - 2581.1)\ \text{kJ/kg} = 7.00\ \text{kJ/kg}$$

and if you assume C_p is essentially constant over the small temperature range indicated by the subscripts, then

$$C_p \cong \frac{\Delta H}{\Delta T} = \frac{7.00\ \text{kJ}}{\text{kg}}\bigg|\frac{}{3.9\Delta°\text{C}} = 1.79\frac{\text{kJ}}{(\text{kg})(\Delta°\text{C})}$$

What are the units of the heat capacity? From the definitions of heat capacity you can see that the units are (energy)/(temperature difference) (mass or moles). The common units found in engineering practice are (we suppress the Δ symbol)

$$\frac{\text{J}}{(\text{kg mol})(\text{K})} \qquad \frac{\text{cal}}{(\text{g mol})(°\text{C})} \qquad \frac{\text{Btu}}{(\text{lb mol})(°\text{F})}$$

Because of the definition of the calorie or Btu, the heat capacity can be expressed in certain different systems of units and still have the same numerical value; for example, heat capacity may be expressed in the units of

$$\frac{\text{cal}}{(\text{g mol})(°\text{C})} = \frac{\text{kcal}}{(\text{kg mol})(°\text{C})} = \frac{\text{Btu}}{(\text{lb mol})(°\text{F})}$$

and still have the same numerical value.

Alternatively, heat capacity may be in terms of

$$\frac{\text{cal}}{(\text{g})(°\text{C})} = \frac{\text{Btu}}{(\text{lb})(°\text{F})} \qquad \text{or} \qquad \frac{\text{J}}{(\text{kg})(\text{K})}$$

Note that

$$\frac{1\ \text{Btu}}{(\text{lb})(°\text{F})} = \frac{4.184\ \text{J}}{(\text{g})(\text{K})}$$

and that the heat capacity of water in the SI system is 4184 J/(kg)(K) at 17°C. These relations are worth memorizing.

Figure 4.5 illustrates the behavior of the heat capacity of a pure substance over a wide range of absolute temperatures. Observe that at zero degrees absolute the heat

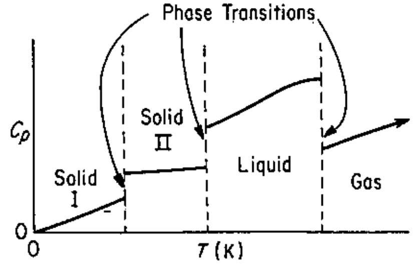


Figure 4.5 Heat capacity as a function of temperature for a pure substance.

capacity is zero. As the temperature rises, the heat capacity also increases until a certain temperature is reached at which a phase transition takes place. The phase transitions are shown also on a related *p–T* diagram in Fig. 4.6 for water. The phase transition may take place between two solid states, or between a solid and a liquid state, or between a solid and a gaseous state, or between a liquid and a gaseous state. Figure 4.5 shows first a transition between solid state I and solid state II, then the transition between solid state II and the liquid state, and finally the transition between the liquid and the gaseous state. Note that the heat capacity is a continuous function *only* in the region between the phase transitions; consequently, it is not possible to have a heat capacity equation for a substance that will go from absolute zero up to any desired temperature. What an engineer does is to determine experimentally the heat capacity between the temperatures at which the phase transitions occur, fit the data with an equation, and then determine a new heat capacity equation for the next range of temperatures between the succeeding phase transitions.

Experimental evidence indicates that the heat capacity of a substance is not constant with temperature, although at times we may assume that it is constant in order to get approximate results. For the ideal monoatomic gas, of course, the heat capacity at constant pressure is constant even though the temperature varies (see Table 4.1). For typical real gases, see Fig. 4.7; the heat capacities shown are for pure components.

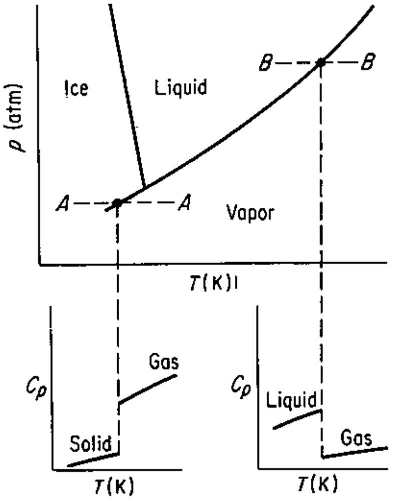


Figure 4.6 Heat capacity and phase transitions.

TABLE 4.1 Heat Capacities of Ideal Gases

Type of molecule	Approximate heat capacity*, C_p	
	High temperature (translational, rotational, and vibrational degrees of freedom)	Room temperature (translational and rotational degrees of freedom only)
Monoatomic	$\frac{5}{2}R$	$\frac{5}{2}R$
Polyatomic, linear	$(3n - \frac{3}{2})R$	$\frac{7}{2}R$
Polyatomic, nonlinear	$(3n - 2)R$	$4R$

*n, number of atoms per molecule; R, gas constant defined in Sec. 3.1.

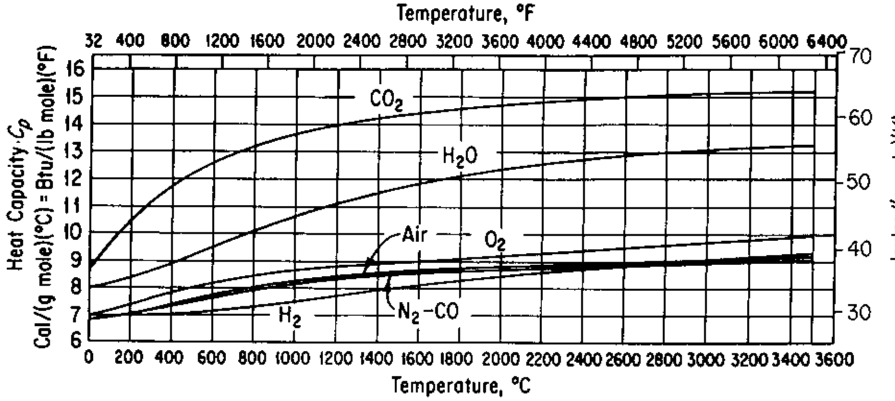


Figure 4.7 Heat capacity curves for the combustion gases.

For ideal gas mixtures, the heat capacity (per mole) of the mixture is the mole weighted average of the heat capacities of the components:

$$C_{p_{\text{avg}}} = \sum_{i=1}^{n} x_i C_{p_i} \tag{4.9}$$

For nonideal mixtures, particularly liquids, you should refer to experimental data or some of the estimation techniques listed in the literature (see the supplementary references at the end of chapter). Also, refer to Sec. 4.8 for details regarding mixtures.

Most of the equations for the heat capacities of solids, liquids, and gases are empirical. We usually express the heat capacity at constant pressure C_p as a function of temperature in a power series, with constants a, b, c, and so on; for example,

$$C_p = a + bT$$

or

$$C_p = a + bT + cT^2$$

where the temperature may be expressed in degrees Celsius, degrees Fahrenheit, degrees Rankine, or degrees kelvin. If C_p is expressed in the form of

$$C_p = a + bT + cT^{-1/2}$$

$$C_p \doteq a + bT - cT^{-2}$$

or a form such that you divide by T, then it is necessary to use kelvin or degrees Rankine in the heat capacity equations, because if degrees Celsius or Fahrenheit were to be used, you might divide at some point in the temperature range by zero. Since these heat capacity equations are valid only over moderate temperature ranges, it is possible to have equations of different types represent the experimental heat capacity data with almost equal accuracy. The task of fitting heat capacity equations to heat capacity data is greatly simplified by the use of digital computers, which can determine the constants of best fit by means of a standard prepared program and at the same time determine how precise the predicted heat capacities are. Heat capacity information can be found in Appendix E. The change of C_p with pressure at high pressures is beyond the scope of our work here. Sources of heat capacity data can be found in several of the references listed at the end of the chapter.

Specific heat is a term often considered synonymous with heat capacity, but this connotation has arisen from loose usage. In principle, specific heat is the ratio of the heat capacity of a substance to the heat capacity of a reference substance, such as

$$\frac{C_{p_A}}{C_{p_{H_2O}}} = \frac{\text{Btu}/(\text{lb}_A)(°\text{F})}{\text{Btu}/(\text{lb}_{H_2O})(°\text{F})}$$

The reference substance temperature must be specified. Because water has a heat capacity of 1.00 Btu/(lb)(°F) at about 17°C, numerical values of specific heats and heat capacities in the American engineering and thermochemical systems are about the same, although their units are not.

EXAMPLE 4.5 Heat Capacity Equation

The heat capacity equation for CO_2 gas is

$$C_p = 6.393 + 10.100T \times 10^{-3} - 3.405T^2 \times 10^{-6}$$

with C_p expressed in cal/(g mol)(ΔK) and T in K. Convert this equation into a form so that the heat capacity will be expressed over the entire temperature range in

(a) Cal/(g mol)(Δ°C) with T in °C
(b) Btu/(lb mol)(Δ°F) with T in °F
(c) J/(kg mol)(ΔK) with T in K

Solution

Changing a heat capacity equation from one set of units to another is merely a problem in the conversion of units. Each term in the heat capacity equation must have the same units as the left-hand side of the equation. To avoid confusion in the conversion, you must remember to distinguish between the temperature symbols that represent temperature and the temperature symbols that represent temperature difference even though the same symbol often is used for each concept. In the conversions below we shall distinguish between the temperature and the temperature difference for clarity.

(a) The heat capacity equation with T in °C and ΔT in Δ°C is

$$C_p \frac{\text{cal}}{(\text{g mol})(\Delta°\text{C})} = 6.393 \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})}\Big|\frac{1\ \Delta\text{K}}{1\ \Delta°\text{C}}$$

$$+\ 10.1000 \times 10^{-3} \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})(\text{K})}\Big|\frac{1\ \Delta\text{K}}{1\ \Delta°\text{C}}\Big|\frac{(T_{°\text{C}} + 273)\ \text{K}}{}$$

$$-3.405 \times 10^{-6} \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})(\text{K})^2}\Big|\frac{1\ \Delta\text{K}}{1\ \Delta°\text{C}}\Big|\frac{(T_{°\text{C}} + 273)^2\ \text{K}^2}{}$$

$$= 6.393 + 10.100 \times 10^{-3} T_{°\text{C}} + 2.757 - 3.405 \times 10^{-6} T_{°\text{C}}^2$$

$$-1.860 \times 10^{-3} T_{°\text{C}} - 0.254$$

$$= 8.896 + 8.240 \times 10^{-3} T_{°\text{C}} - 3.405 \times 10^{-6} T_{°\text{C}}^2$$

(b)

$$C_p \frac{\text{Btu}}{(\text{lb mol})(\Delta°\text{F})} = 6.393 \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})}\Big|\frac{454\ \text{g mol}}{1\ \text{lb mol}}\Big|\frac{1\ \text{Btu}}{252\ \text{cal}}\Big|\frac{1\ \Delta\text{K}}{1.8\ \Delta°\text{F}}$$

$$+\ 10.100 \times 10^{-3} \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})(\text{K})}\Big|\frac{454\ \text{g mol}}{1\ \text{lb mol}}\Big|\frac{1\ \text{Btu}}{252\ \text{cal}}\Big|\frac{1\ \Delta\text{K}}{1.8\ \Delta°\text{F}}\Big|\frac{\left(273 + \dfrac{T_{°\text{F}} - 32}{1.8}\right)\text{K}}{}$$

$$-3.405 \times 10^{-6} \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})(\text{K})^2}\Big|\frac{454\ \text{g mol}}{1\ \text{lb mol}}\Big|\frac{1\ \text{Btu}}{252\ \text{cal}}\Big|\frac{1\ \Delta\text{K}}{1.8\ \Delta°\text{F}}\Big|\frac{\left(273 + \dfrac{T_{°\text{F}} - 32}{1.8}\right)^2 \text{K}^2}{}$$

$$= 6.393 + 10.100 \times 10^{-3}[273 + (T_{°\text{F}} - 32)/1.8]$$

$$-3.405 \times 10^{-6}[273 + (T_{°\text{F}} - 32)/1.8]^2$$

$$= 6.393 + 2.575 + 5.61 \times 10^{-3} T_{°\text{F}} - 0.222$$

$$-0.964 \times 10^{-3} T_{°\text{F}} - 1.05 \times 10^{-6} T_{°\text{F}}^2$$

$$= 8.746 + 4.646 \times 10^{-3} T_{°\text{F}} - 1.05 \times 10^{-6} T_{°\text{F}}^2$$

Note: $T_\text{K} = 273 + \dfrac{T_{°\text{F}} - 32}{1.8}$.

(c)

$$C_p \frac{\text{J}}{(\text{kg mol})(\Delta\text{K})} = 6.393 \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})}\Big|\frac{4.184\ \text{J}}{1\ \text{cal}}\Big|\frac{1000\ \text{g}}{1\ \text{kg}}$$

$$+\ 10.1000 \times 10^{-3} \frac{\text{cal}}{(\text{g mol})(\Delta\text{K})(\text{K})}\Big|\frac{4.184\ \text{J}}{1\ \text{cal}}\Big|\frac{1000\ \text{g}}{1\ \text{kg}}\Big|\frac{(T_\text{K})\text{K}}{}$$

$$-3.405 \times 10^{-6} \frac{\text{cal}}{(\text{g mol})(\text{K})^2(\Delta\text{K})}\Big|\frac{4.184\ \text{J}}{1\ \text{cal}}\Big|\frac{1000\ \text{g}}{1\ \text{kg}}\Big|\frac{(T_\text{K}^2)\text{K}^2}{}$$

$$= 2.675 \times 10^4 + 42.27 T_\text{K} - 1.425 \times 10^{-2} T_\text{K}^2$$