PROBLEM SOLVING

Thermodynamics

1. Define the **system** you are dealing with; distinguish the system under study from its surroundings.
2. When applying the first law of thermodynamics, be careful of **signs** associated with **work** and **heat**. In the first law, work done *by* the system is positive; work done *on* the system is negative. Heat *added* to the system is positive, but heat *removed* from it is negative. With heat engines, we usually consider the heat intake, the heat exhausted, and the work done as positive.
3. Watch the **units** used for work and heat; work is most often expressed in joules, and heat can be in calories, kilocalories, or joules. Be consistent: choose only one unit for use throughout a given problem.
4. **Temperatures** must generally be expressed in kelvins; temperature *differences* may be expressed in C° or K.
5. **Efficiency** (or coefficient of performance) is a ratio of two energy transfers: useful output divided by required input. Efficiency (but *not* coefficient of performance) is always less than 1 in value, and hence is often stated as a percentage.
6. The **entropy** of a system increases when heat is added to the system, and decreases when heat is removed. If heat is transferred from system A to system B, the change in entropy of A is negative and the change in entropy of B is positive.

Summary

The **first law of thermodynamics** states that the change in internal energy ΔU of a system is equal to the heat *added* to the system, Q, minus the work done *by* the system, W:

$$\Delta U = Q - W. \qquad \textbf{(15–1)}$$

This important law is a statement of the conservation of energy, and is found to hold for all processes.

An **isothermal** process is a process carried out at constant temperature.

In an **adiabatic** process, no heat is exchanged ($Q = 0$).

The work W done by a gas at constant pressure P is given by

$$W = P\,\Delta V, \qquad \textbf{(15–3)}$$

where ΔV is the change in volume of the gas.

A **heat engine** is a device for changing thermal energy, by means of heat flow, into useful work.

The **efficiency** e of a heat engine is defined as the ratio of the work W done by the engine to the high temperature heat input Q_H. Because of conservation of energy, the work output equals $Q_H - Q_L$, where Q_L is the heat exhausted at low temperature to the environment; hence

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}. \qquad \textbf{(15–4)}$$

Q_H, Q_L, and W, as defined for heat engines, are positive.

The *upper limit* on the efficiency (the *Carnot efficiency*) can be written in terms of the higher and lower operating temperatures (in kelvins) of the engine, T_H and T_L, as

$$e_{\text{ideal}} = 1 - \frac{T_L}{T_H}. \qquad \textbf{(15–5)}$$

Real (irreversible) engines always have an efficiency less than this.

The operation of **refrigerators** and **air conditioners** is the reverse of a heat engine: work is done to extract heat Q_L from a cool region and exhaust it to a region at a higher temperature. The coefficient of performance (COP) for either is

$$\text{COP} = \frac{Q_L}{W}, \qquad \begin{bmatrix}\text{refrigerator or}\\ \text{air conditioner}\end{bmatrix} \qquad \textbf{(15–6a)}$$

where W is the work needed to remove heat Q_L from the area with the low temperature.

A **heat pump** uses work W to bring heat Q_L from the cold outside and deliver heat Q_H to warm the interior. The coefficient of performance of a heat pump is

$$\text{COP} = \frac{Q_H}{W}, \qquad [\text{heat pump}] \qquad \textbf{(15–7)}$$

because it is the heat Q_H delivered inside the building that counts.

The **second law of thermodynamics** can be stated in several equivalent ways:

(a) heat flows spontaneously from a hot object to a cold one, but not the reverse;
(b) there can be no 100% efficient heat engine—that is, one that can change a given amount of heat completely into work;
(c) natural processes tend to move toward a state of greater disorder or greater **entropy**.

Statement (c) is the most general statement of the second law of thermodynamics, and can be restated as: the total entropy, S, of any system plus that of its environment increases as a result of any natural process:

$$\Delta S > 0. \qquad \textbf{(15–9)}$$

The change in entropy in a process that transfers heat Q at a constant temperature T is

$$\Delta S = \frac{Q}{T}. \qquad \textbf{(15–8)}$$

Entropy is a quantitative measure of the **disorder** of a system. The second law of thermodynamics also indicates that as time goes on, energy is **degraded** to less useful forms—that is, it is less available to do useful work.

The second law of thermodynamics tells us in which direction processes tend to proceed; hence entropy is called "time's arrow."

[*Entropy can be examined from a statistical point of view, considering **macrostates** (for example, P, V, T) and **microstates** (state of each molecule). The most probable processes are the ones we observe. They are the ones that increase entropy the most. Processes that violate the second law "could" occur, but only with *extremely* low probability.]

[*All heat engines give rise to **thermal pollution** because they exhaust heat to the environment.]