## Work Done by a System

The **work done by a system** ($\Delta W$) is positive if the system thereby loses energy to its surroundings. When the surroundings do work *on* the system so as to give it energy, $\Delta W$ is a negative quantity. In a small expansion $\Delta V$, a fluid at constant pressure P does work given by

$$\Delta W = P\,\Delta V$$

## First Law of Thermodynamics

The **First Law of Thermodynamics** is a statement of the law of conservation of energy. It states that if an amount of heat ($\Delta Q$) flows into a system, then this energy must appear as increased internal energy $\Delta U$ for the system and/or work $\Delta W$ done *by* the system on its surroundings. As an equation, the First Law is

$$\Delta Q = \Delta U + \Delta W$$

## Thermodynamic Processes

An **isobaric process** is a process carried out at constant pressure.

An **isovolumic process** is a process carried out at constant volume. When a gas undergoes such a process,

$$\Delta W = P\,\Delta V = 0$$

and so the First Law of Thermodynamics becomes

$$\Delta Q = \Delta U$$

Any heat that flows into the system appears as increased internal energy of the system.

An **isothermal process** is a constant-temperature process. In the case of an ideal gas where the constituent atoms or molecules do not interact when separated, $\Delta U = 0$ in an isothermal process. However, this is not true for many other systems. For example, $\Delta U \neq 0$ as ice melts to water at $0^{\circ}$C, even though the process is isothermal.

For an ideal gas, $\Delta U = 0$ is an isothermal change, and so the First Law becomes

$$\Delta Q = \Delta W \qquad \text{(ideal gas)}$$

For an ideal gas changing isothermally from $(P_1, V_1)$ to $(P_2, V_2)$, where $P_1 V_1 = P_2 V_2$,

$$\Delta Q = \Delta W = P_1 V_1 \ln \left(\frac{V_2}{V_1}\right) = 2.30\, P_1 V_1 \log \left(\frac{V_2}{V_1}\right)$$

Here, ln and log are logarithms to the base e and base 10, respectively.

## Adiabatic Process

An **adiabatic process** is one in which no heat is transferred to or from the system. For such a process, $\Delta Q = 0$. Hence, in an adiabatic process, the first law becomes

$$0 = \Delta U + \Delta W$$

Any work done by the system is done at the expense of the internal energy. Any work done on the system serves to increase the internal energy.

For an ideal gas changing from conditions $(P_1, V_1, T_1)$ to $(P_2, V_2, T_2)$ in an adiabatic process,

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \text{ and } T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

where $\gamma = c_p/c_n$ is discussed below.

## Specific Heats of Gases

When a gas is heated *at constant volume*, the heat supplied goes to increase the internal energy of the gas molecules. But when a gas is

The *Carnot cycle* is the most efficient cycle possible for a heat engine. An engine that operates in accordance to this cycle between a hot reservoir ($T_h$) and a cold reservoir ($T_c$) has efficiency

$$\text{efficiency}_{\text{max}} = 1 - \frac{T_c}{T}$$

Kelvin temperatures must be used in this equation.

# Entropy and the Second Law

## Second Law of Thermodynamics

The **Second Law of Thermodynamics** can be stated in three equivalent ways:

(1) Heat flows spontaneously from a hotter to a colder object, but not vice versa.

(2) No heat engine that cycles continuously can change all its heat-in to useful work-out.

(3) If a system undergoes spontaneous change, it will change in such a way that its entropy will increase or, at best, remain constant.

**Note!**

The Second Law tells us the manner in which a spontaneous change will occur, while the First Law tells us whether or not the change is possible. The First Law deals with the conservation of energy; the Second Law deals with the dispersal of energy.

heated *at constant pressure*, the heat supplied not only increases the internal energy of the molecules but also does mechanical work in expanding the gas against the opposing constant pressure. Hence the specific heat of a gas at constant pressure $c_p$ is greater than its specific heat at constant volume, $c_v$. It can be shown that, for an ideal gas of molecular mass M,

$$c_p - c_v = \frac{R}{M} \qquad (\text{ideal gas})$$

where R is the universal gas constant. In the SI, R = 8314 J/kmol K and M is in kg/kmol; then $c_p$ and $c_v$ must be in J/kg K = J/kg °C. Some people use R = 1.98 cal/mol • °C and M in g/mol, in which case $c_p$ and $c_v$ are in cal/g • °C.

**Specific heat ratio** ($\gamma = c_p / c_v$): As discussed above, this ratio is greater than unity for a gas. The kinetic theory of gases indicates that for monatomic gases (such as He, Ne, Ar), $\gamma = 1.67$. For diatomic gases (such as $O_2$, $N_2$), $\gamma = 1.40$ at ordinary temperatures.

## P–V Diagrams

Work is related to area in a P–V diagram. The work done by a fluid in an expansion is equal to the area beneath the expansion curve on a P–V diagram. In a cyclic process, the work output per cycle done by a fluid is equal to the area enclosed by the P–V diagram representing the cycle.

## Efficiency of a Heat Engine

The **efficiency of a heat engine** is defined as

$$\text{efficiency} = \frac{\text{work output}}{\text{heat input}}$$

## Entropy

**Entropy** (S) is a *state variable* for a system in equilibrium. By this is meant that S is always the same for the system when it is in a given equilibrium state. Like P, V, and U, the entropy is a characteristic of the system at equilibrium.

When heat $\Delta Q$ enters a system at an absolute temperature T, the resulting change in entropy of the system is

$$\Delta S = \frac{\Delta Q}{T}$$

provided the system changes in a reversible way. The SI unit for entropy is J/K.

A *reversible change* (or process) is one in which the values of P, V, T, and U are well defined during the change. If the process is reversed, then P, V, T, and U will take on their original values when the system is returned to where it started. To be reversible, a process must usually be slow, and the system must be close to equilibrium during the entire change.

Another, fully equivalent, definition of entropy can be given from a detailed molecular analysis of the system. If a system can achieve a particular state (i.e., particular values of P, V, T, and U) in $\Omega$ (omega) different ways (different arrangements of the molecules, for example), then the entropy of the state is

$$S = k_B \ln \Omega$$

where ln is the logarithm to base e, and $k_B$ is Boltzmann's constant, $1.38 \times 10^{-23}$ J/K.

## Entropy Is a Measure of Disorder

A state that can occur in only one way (one arrangement of its molecules, for example) is a state of high order. But a state that can occur in many ways is a more disordered state. One way to associate a number with disorder is to take the disorder of a state as being proportional to $\Omega$, the number of ways the state can occur. Because $S = k_B \ln \Omega$, entropy is a measure of disorder.

Spontaneous processes in systems that contain many molecules always occur in a direction from a

$$\left(\begin{array}{c}\text{state that can exist}\\ \text{in only a few ways}\end{array}\right) \rightarrow \left(\begin{array}{c}\text{state that can exist}\\ \text{in many ways}\end{array}\right)$$

Hence, when left to themselves, systems retain their original state of order or else increase their disorder.

The most probable state of a system is the state with the largest entropy. It is also the state with the most disorder and the state that can occur in the largest number of ways.

# Solved Problems

**Solved Problem 3.1** A 20 g piece of aluminum ($c = 0.21$ cal/g °C) at 90 °C is dropped into a cavity in a large block of ice at 0 °C. How much ice does the aluminum melt?

**Solution.**

(heat change of Al as it cools to 0 °C)
+ (heat change of mass m of ice melted) = 0

$$(m\ c\ \Delta T)_{Al} + (H_f m)_{ice} = 0$$

$$(20\ \text{g})(0.21\ \text{cal/g}\ ^\circ\text{C})(0\ ^\circ\text{C} - 90\ ^\circ\text{C}) + (80\ \text{cal/g})\ m = 0$$

from which $m = 4.7$ g is the quantity of ice melted.

**Solved Problem 3.2** What is the net work output per cycle for the thermodynamic cycle in Figure SP3-1?

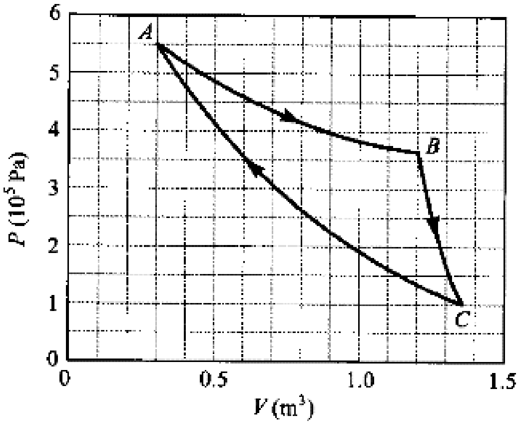

**Figure SP3-1**

**Solution.** We know that the net work output per cycle is the area enclosed by the P-V diagram. We estimate that in area ABCA there are 22 squares, each of area

$(0.5 \times 10^5 \text{ N/m}^2)(0.1 \text{ m}^3) = 5 \text{ kJ}$

Therefore,

Area enclosed by cycle $\approx (22)(5 \text{ kJ}) = 110 \text{ kJ}$