

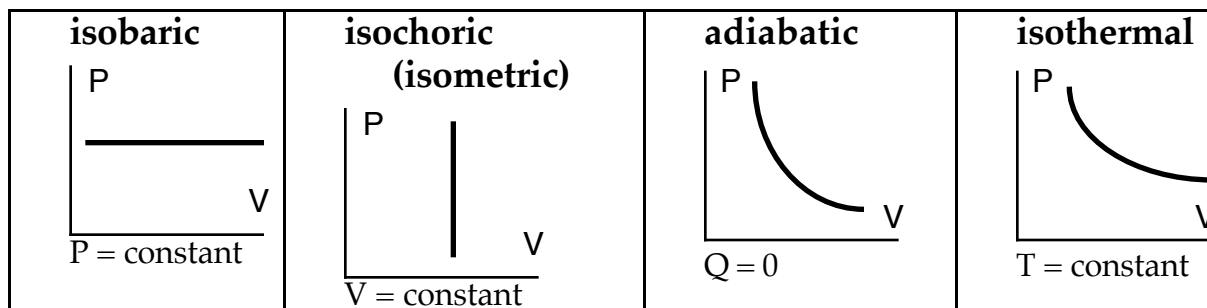
Chapter 18 The Laws of Thermodynamics

Section 18.2

- Thermodynamics studies the way in which internal energy, work, and heat are related in systems. What is meant by the word “system” is usually obvious in the problems encountered at this level. The process of solving thermodynamic problems requires separating the “system” from “the rest of the universe” in order to understand: 1) where heat is flowing to ($Q = +$) or from ($Q = -$), and 2) what is doing work ($W = +$) or being worked upon ($W = -$).
- The first law of thermodynamics can be expressed in terms of the internal energy, the heat, and the work: $\Delta U = Q - W$. In this expression, work done by the system is considered positive and heat absorbed by the system is considered negative.

Section 18.3

- Work is done on or by a gas when its volume changes ($W = P \Delta V$ calculates the work done when the pressure is constant). Even if the pressure is not constant, the work done is given by the area underneath the curve on the P versus V graph. If the path goes clockwise, the work done is positive. If the path goes counterclockwise, the work done is negative. When a gas goes through a cycle, then the *net* work (equal to the area within the closed path on the P versus V graph) must be calculated.
- A number of different processes can be performed on gases. These processes are identified by what factor stays constant or is equal to zero. Note that adiabats are “steeper” than isotherms.



Section 18.4

- The product of the molecular mass times the specific heat is equal to the molar specific heat ($C = M c$). The molar specific heat (just as for the specific heat) depends on whether the process is constant volume or constant pressure. These are related by: $C_p - C_v = R$ and $C_v = \frac{3}{2} R$.
- The total internal energy of a gas is given by $U = \frac{3}{2} nRT$ and the change in internal energy by $\Delta U = \frac{3}{2} nR \Delta T$. Note that for an ideal gas, $nRT = PV$, so that $U = \frac{3}{2} PV$.
- The work done by a thermodynamic system (as well as the heat absorbed or liberated) depends on the path followed on the P–V graph. For example, the heat absorbed in a constant pressure process ($Q = n C_p \Delta T$) is different than the heat absorbed in a constant volume process ($Q = n C_v \Delta T$). However, the change in internal energy ΔU **does not**

depend on the path followed. As shown in the previous paragraph, ΔU only depends on ΔT .

Section 18.5

- The second law of thermodynamics can be expressed several ways: 1) The spontaneous flow of heat is always from a higher temperature object to a lower temperature object, 2) Kelvin-Planck: no heat engine may operate without exhausting some thermal energy, 3) Clausius: heat cannot flow from a cold to a hot reservoir without work being performed, or 4) Clausius: the entropy of isolated systems naturally can only increase.

Section 18.6

- The efficiency of thermodynamic systems (and heat engines in particular) is defined as the work done by the system divided by the heat put into the system $\left(e = \frac{W}{Q_h} \right)$. For a heat engine operating between a higher temperature reservoir and a cooler temperature reservoir, the efficiency can be expressed as $e = 1 - \frac{Q_c}{Q_h}$. For the ideal highest efficiency Carnot engine $\left(\text{where } \frac{T_c}{T_h} = \frac{Q_c}{Q_h} \right)$, this becomes $e_C = 1 - \frac{T_c}{T_h}$.

Section 18.7

- For refrigerators, air conditioners, and heat pumps, we calculate the coefficient of performance (COP) rather than the efficiency. For a refrigerator or an air conditioner, this is $\text{COP} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}$. One can calculate Carnot efficiencies for refrigerators or air conditioners as well using $\frac{T_c}{T_h} = \frac{Q_c}{Q_h}$.

Section 18.8

- The concept of entropy was designed to predict the direction in which natural processes occur (e.g. heat flowing from hot to cold). Typically only changes in entropy are important $\left(\Delta S = \frac{Q}{T} \right)$ calculated at particular temperature T . Entropy changes can be calculated when mixing materials at different temperatures (actually an irreversible process), but the average temperature for each material must be used when calculating its ΔS .

Section 18.9

- Entropy is also statistically related to the order of a system ($S = k \ln W$): an increase in entropy means that the system has become less ordered, i.e. more disordered.

Section 18.10

- The third law of thermodynamics says that absolute zero cannot be achieved in a finite number of steps (i.e., is thus impossible to achieve.)