

The 1st Law of Thermodynamics

This law is a restatement of the law of conservation of energy.

$$\Delta U = Q + W$$

- ΔU represents the net change in the internal energy of the gas
- Q represents the net heat added (+) or removed (-) from a confined gas
- W is work done by the confined gas (+) or on the confined gas (-)

For a gas, the change in its internal energy, ΔU , is directly proportional to the change in its temperature measured in Kelvin. This means that ΔU only reflects a change in the kinetic energy of the gas molecules. The potential energy cannot change except when there is a phase change: liquid to solid or liquid to vapor.

The current statement of this law places an emphasis on the internal energy of the gas. The law states that the internal energy of a gas can be increased in one of two ways: by the addition of heat or by work being done on the system by an external agent. Remember that during compressions, as the volume of the gas decreases its temperature (except in isothermal processes) increases - representing a subsequent increase in the internal energy of the system. Thus work done on the system by an external agent as the piston is pressed down causing the volume to decrease is negative. Conversely, if the gas expands the piston, work is positive since the internal energy of the gas decreases as the temperature decreases.

2nd Law of Thermodynamics

If an isolated system is permitted to undergo spontaneous change, it changes in such a way that its disorder increases, or at best, remains the same. In thermal equilibrium, there is no tendency to want to change, since the temperatures are equal. This condition is a state of maximum disorder; there is no natural way to re-establish the original temperature differential.

A measure of this disorder is called entropy, S . It is measured in J/K.

$$\Delta S = Q/T$$

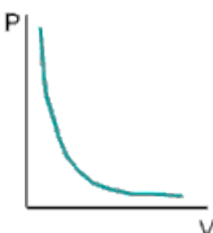
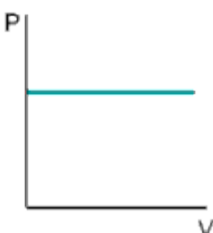
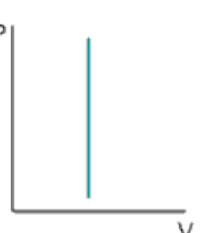
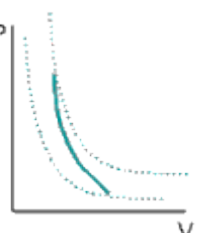
An alternative statement of the second law is that heat only flows spontaneously from a hot object to a cold object and never in the opposite direction.

Four Gas Processes

To aid in our understanding of the 1st and 2nd Laws of Thermodynamics, we will begin with a listing of the properties of the four fundamental gas processes: isothermal, isobaric, isovolumetric, and adiabatic.

An **isothermal process** means that the temperature of the gas does not change during the expansion or compression. An **isobaric process** means that the pressure of the gas does not change while in an **isovolumetric (isochoric) process** the volume remains constant. An **adiabatic process** is one in which no heat is added to or removed from the system. Adiabatic processes can occur in thermally isolated systems or spontaneously, as in the rapid expansion of a compressed gas when sprayed out of an aerosol can or in the rapid compression of air in a bicycle pump.

The following table highlights eight important properties of each process. C_p and C_v represent the molar specific heats of a gas when held at either a constant pressure or a constant volume. They equal the amount of heat, in joules, needed to raise one mole of the gas 1°C .

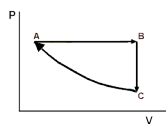
	isothermal	isobaric	isochoric	adiabatic
held constant	temperature	pressure	volume	heat
combined gas law	$P_1V_1 = P_2V_2$	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
PV diagrams				
$W = - \int P dV$ expanding + -compressed	$W = nRT [\ln(V_2 \div V_1)]$	$W = P\Delta V$	0	$W = \Delta U$
Q - temp dec + temp inc	$Q = -W$	$Q = nC_p\Delta T$	$Q = nC_v\Delta T$	0
ΔU - temp dec + temp inc	0	$\Delta U = nC_v\Delta T$	$\Delta U = nC_v\Delta T$	$\Delta U = nC_v\Delta T$
1st Law	$\Delta U = Q + W$ $\Delta U = 0$ $Q = -W$ as the gas expands, heat must be added	$\Delta U = Q + W$ $nC_v\Delta T = nC_p\Delta T - P\Delta V$ since $P\Delta V = nR\Delta T$ $nC_v\Delta T = nC_p\Delta T - nR\Delta T$ $C_p = C_v + nR$	$\Delta U = Q + W$ $\Delta U = Q$ since no work is done, the internal energy of the gas increases with the addition of heat	$\Delta U = Q + W$ $\Delta U = W$ since no heat can be added or removed, any work done is at the expense of the internal energy of the gas
ΔS	$\Delta S = nR [\ln(V_2 \div V_1)]$	$\Delta S = nC_p [\ln(T_2 \div T_1)]$	$\Delta S = nC_v [\ln(T_2 \div T_1)]$	0

State Variables

When examining PV graphs, state variables are ones that always maintain a constant value at a given position on a PV graph. These variables are:

P, V, T, U, and S

Recall from the ideal gas law that $PV = nRT$. If n , the amount of gas, does not change, then $PV \propto T$. We can use this relationship to determine how the temperatures at different positions on a PV-diagram would compare. For example, on the PV-diagram shown below, we can determine that the temperature at point A is lower than the temperature at point B by comparing their "PV" products. Since the volume at point A is smaller than the volume at point B, A's "PV" product would be less than the "PV" product for point B. Note that the same type of argument could tell us that the temperature at point C is also lower than that at point B since C's "PV" product would be less than B's because of C's lower pressure value. We cannot compare the temperatures at point A and point C without having specific scales on the x- and y-axes.



Since the internal energy of a gas is directly proportional to its temperature, we can conclude that the internal energy of the gas at point B is greater than at either points A or C.

When the gas expands isobarically along path AB, the internal energy of the gas should decrease. Since the temperature at point B is higher, we know that heat must have been added to the system. During the isochoric process BC, no work was done on the gas since its volume remained unchanged. However, we know that heat must have been released from the system since the temperature at point C is less than that at point B. The final compression along path CA returns the gas to its starting position, that is, to its original state values of pressure, volume, temperature, internal energy, and entropy. As a general rule of thumb, you can compare the entropies at two positions by knowing whether heat has been added (S increases) or heat has been removed (S decreases). In our diagram, entropy increased along path AB and decreased along path BC.

Note that heat (Q) and work (W) are NOT state variables. Heat is the energy transferred between states - from a warm body to a cooler body as a result of their temperature differential. Work is done whenever the energy content of a system changes.

For the closed path, ABCA, the first law reduces to $Q = -W$ since $\Delta U = 0$. Don't forget that changes in all state variables (ΔP , ΔV , ΔT , and ΔS) are also equal to 0 whenever you make a complete cycle around a PV diagram.