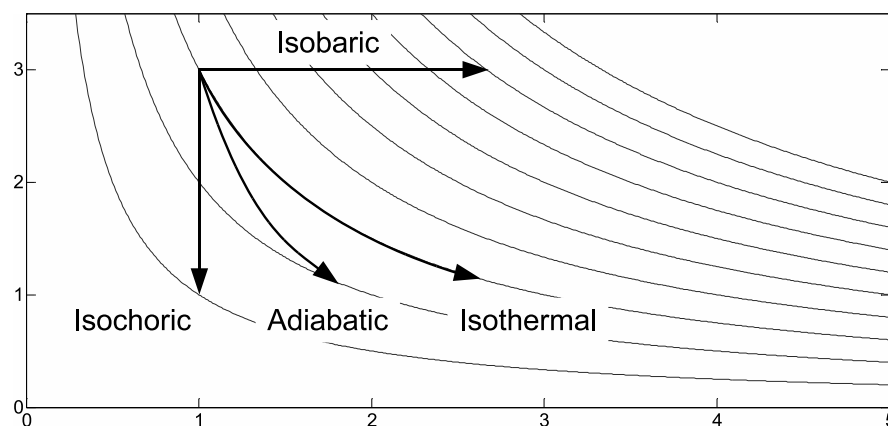


Thermodynamic Processes

Common Processes

In the previous lecture we discussed the definition of thermodynamic work and the first law of thermodynamics. I also introduced the PV diagram as a useful tool for studying ideal gas processes. The figure below shows a PV diagram with a number of lines that represent **isotherms**, or lines of constant temperature (and therefore constant energy). As you discovered in lab, there is an inverse relationship between pressure and volume along these lines: $P = (nRT)/V$. I find it very useful to picture isotherms on PV diagrams because they represent good reference points for temperature and energy. (In the graph below, the units of pressure and temperature are arbitrary, but common units on this scale in the lab are *atmospheres* and *bars* for pressure, and *liters* for volume. None of these are SI units!)



The graph shows a number of common ideal gas processes. They are typically defined by what is constant.

Isobaric

These processes proceed at constant pressure (horizontal lines on a PV diagram). It is particularly easy to compute the work for isobaric processes: $W = P\Delta V$. Notice from the diagram that an isobaric expansion of an ideal gas is always associated with an increase in temperature and thermal energy. This is despite the fact that the gas does work on its surroundings, which means that the gas loses energy through work. We can conclude, therefore, that heat must be absorbed in an isobaric expansion, and that more heat is absorbed than work is done.

For an isobaric *compression*, which would be directed leftward in the diagram, the gas does negative work. This means that energy is added to the gas through work. However, the temperature and energy decrease, so the process must give off more heat than it gains through work.

Isochoric

These processes proceed at constant volume (vertical curves on a PV diagram). For an isochoric (or *isovolumetric*) process, no work is done by or on the gas. (The area under an isochoric curve is zero.) Therefore, the change in energy of the gas is completely due to the heat added or taken away: $\Delta U = Q$. We call an isochoric increase in pressure **isochoric heating**, and a decrease in pressure **isochoric cooling**.

Isothermal

These processes proceed at constant temperature. On a PV diagram, such processes follow the curved isothermal lines in which pressure is inversely proportional to volume. In an isothermal process, thermal energy is also constant, so $\Delta U = 0$ and $Q = W$; all heat added is converted to work, and vice versa. Since no work can be done isothermally without heat being exchanged with the surroundings, isothermal processes are usually performed in containers with highly conducting walls that are held in a constant temperature heat bath (a heat “reservoir”).

Isothermal processes are characterized by the expression $P_i V_i = P_f V_f$, or $PV = \text{constant}$. Using $P = (nRT)/V$ and doing a little calculus, we find that

$$W = \int_{V_i}^{V_f} P dV = nRT \ln \left(\frac{V_f}{V_i} \right) = Q .$$

When we discuss heat capacities below we will see a different way to express Q and W for isothermal processes in terms of the change in temperature.

Adiabatic

These processes are characterized by *no heat transfer*. Adiabatic processes are usually performed in highly insulating containers (like thick styrofoam coolers). Alternatively, processes that proceed so quickly that the changes are made before significant heat can be transferred can be considered adiabatic. Because $Q = 0$, the energy change in an adiabatic process is completely due to work $\Delta U = -W$.

For example, consider spraying compressed gas from a spray can (such as hair spray, computer cleaning air, etc.) Even though the thin walls of such a can are good conductors of heat, the sudden expansion of the gas happens quickly enough that we can consider this an example of adiabatic expansion. The gas does positive work on its surroundings and therefore loses energy. The result is that the sprayed air (as well as the air in the can) rapidly drop in temperature.

Adiabatic processes are characterized by the expression $PV^\gamma = \text{constant}$, or

$$P_i V_i^\gamma = P_f V_f^\gamma .$$

Here $\gamma = (f + 2)/f$, where f is the number of degrees of freedom per molecule in the gas. For monatomic gases ($f = 3$), $\gamma = 5/3$, while for diatomic gases that exhibit rotation but not vibration ($f = 5$), $\gamma = 7/5$.

With a little mathematical effort that you should try to follow in your textbook, it turns out that the work done by the gas in an adiabatic process is

$$W = \left(\frac{1}{\gamma - 1} \right) (P_i V_i - P_f V_f) .$$

When we discuss heat capacities below we will see a different way to express ΔU and W for adiabatic processes in terms of the change in temperature.

Here is a summary of what is constant in each of these processes (assuming a constant number of molecules/moles of gas):

- Isobaric: P and V/T are constant
- Isochoric: V and P/T are constant
- Isothermal: T , U , and PV are constant
- Adiabatic: PV^γ is constant

Molar (Specific) Heat Capacities

In the last class you encountered questions comparing the amount of heat you would have to add to a gas to raise its temperature by a specific amount when the gas was held at constant pressure vs. when the gas was held at constant volume. There was a big difference between the two. At constant volume, no work is done by the gas so all of the heat you add goes into the thermal energy of the gas, which corresponds to any increase in temperature. At constant pressure, the gas will expand and do work on its surroundings. This means that when you add heat to the gas, only some of the heat will go into the thermal energy of the gas. The rest will be converted to the work done by the gas on its surroundings.

This means that you need to add more heat at constant pressure than at constant volume to achieve the same change in temperature.

Now recall from our discussion of specific heat and heat capacities that $Q = mc\Delta T$, where c was the specific heat of the substance and mc was the *heat capacity* of an object with mass m and specific heat c .

For ideal gases, the number of molecules (and hence the number of moles) is more important for the thermal properties of the gas than the mass, so let's rewrite our heat equation with that in mind:

$$Q = nC\Delta T,$$

where n is the number of moles of gas in the container, and C is the **molar specific heat capacity** of the gas. (Some books just call this the “molar heat capacity,” but because it's for a specific amount of gas, one mole, it's really a specific heat capacity.)

Recall that we can write $U = (f/2)Nk_B T = (f/2)nRT$ for an ideal gas with f degrees of freedom per molecule. To relate Q to ΔT for an ideal gas, we just need to relate Q and ΔU for that gas using the first law of thermodynamics. Let's consider the molar heat capacities for different processes.

Constant Volume

When the volume of the gas is held constant, $W = 0$ and $Q = \Delta U = (f/2)nR\Delta T$. That means that the **molar specific heat capacity at constant volume** for an ideal gas is $C_V = (f/2)R$. (The subscript V denotes a constant volume process.)

For an ideal gas, $R \approx 8.3 \text{ J/molK}$. This means that, for a monatomic ideal gas or any ideal gas cold enough that there are only the three translational degrees of freedom, $C_V = 12.5 \text{ J/molK}$. For a diatomic gas at room temperature (five degrees of freedom), $C_V = 20.8 \text{ J/molK}$.

Important: The expression $Q = nC_V\Delta T$ is *only true* for ideal gases at *constant volume*, but the expression $\Delta U = nC_V\Delta T$ is *always true* for all ideal gases, *regardless of the process by which the energy changes*. In other words, a better term than “heat capacity at constant volume” is “energy capacity.” For an ideal gas, energy is proportional to temperature, and nC_V is the proportionality constant.

Constant Pressure

For a gas at constant pressure, $W = P\Delta V = nR\Delta T$. Therefore,

$$\Delta Q = \Delta U + W = (f/2)nR\Delta T + nR\Delta T = (1 + f/2)nR\Delta T = nC_P\Delta T .$$

This means that the **molar specific heat capacity at constant pressure** is

$$C_P = (f/2)R + R = \left(\frac{f+2}{2}\right)R , \quad \text{or} \quad C_P = C_V + R .$$

Remember, $C_P > C_V$ because some of the heat must be converted to work in an isobaric process.