

# Chapter 19

## The First Law of Thermodynamics

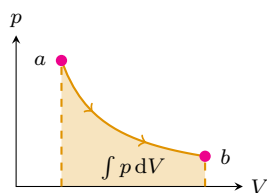
### 19.1 The First Law and Heat Capacity

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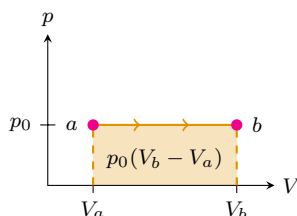
- By the conservation of energy,  $\Delta E_{\text{int}} = Q + W$ . This implies the following.
- **First Law of Thermodynamics:** The following formula, which is analogous to conservation of energy.

$$dE_{\text{int}} = dQ - p dV$$

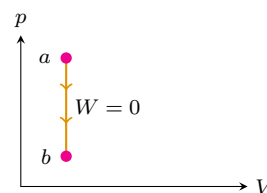
- The work done *by* the gas is the area under the curve defined by the path between two pressure-volume conditions.



(a) Isothermal process.



(b) Isobaric process.



(c) Isochoric process.

Figure 19.1: Work as a geometric integral of a pressure/volume graph.

- Thus, for an isothermal process,  $W = -\int p dV$ .
- For an isobaric process,  $W = -P(V_b - V_a)$ .
- For an isochoric process,  $W = 0$ .
- Two processes of getting from condition *a* to condition *b*:

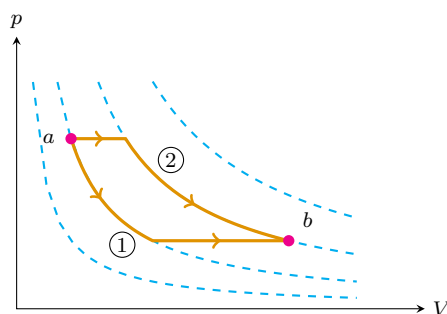


Figure 19.2: Alternate paths.

- We know from the first law that  $\Delta E_{\text{int}}$  is the same for both properties.
- However, from the above, we know that  $W$  is not the same for both (different areas under the curve).
- Thus, by the first law, heat cannot be the same (it must be offset to compensate).

- **Molar heat capacity** (of a gas at constant volume): Defined by the following.

$$C_V = \frac{1}{n} \frac{dQ_V}{dT}$$

- Tells you how much heat you have to add to raise the temperature a certain amount.

- Additionally, since  $dW = 0$  at constant volume,  $dE_{\text{int}} = dQ_V$ .

- Thus,  $C_V = 1/n \cdot dE_{\text{int}}/dT$ .
- Consequently, since  $E_{\text{int}} = \frac{3}{2}nRT$ , we have that  $dE_{\text{int}}/dT = \frac{3}{2}nR$ .
- Therefore, at constant volume,  $C_V = \frac{3}{2}R$ .

- **Molar heat capacity** (of a gas at constant pressure): Defined by the following.

$$C_p = \frac{1}{n} \frac{dQ_p}{dT}$$

- For the same  $dT$ ,  $dQ_p \neq dQ_V$ .

- We know that  $C_p > C_V$ .

- This is principally because of the difference between the equations  $dE_{\text{int}} = dQ$ , pertaining to an isochoric process, and  $dE_{\text{int}} + dW = dQ$ , pertaining to an isobaric process.
- In the former, we can see that the change in internal energy (which is directly related to the temperature for an ideal gas) is directly reflected by the amount of heat flowing into the system.
- However, in the latter, we raise the temperature by the same amount, so internal energy increases by the same amount. However, the gas must expand to maintain its constant pressure. Thus, some work is done. Thus, more heat must flow into the system to account for the work done *and* maintain the same temperature.

- For some  $dT$  (i.e., some  $dE_{\text{int}}$ ).

- Heat added at constant volume:  $dE_{\text{int}} = dQ_V = nC_V dT$ .
- Heat added at constant pressure:  $dE_{\text{int}} = dQ_p - p dV = nC_p dT - p dV$ .
- The amount of heat you add in both cases will be different, but the change in internal energy will be the same.
- Thus,

$$\begin{aligned} nC_V dT &= nC_p dT - p dV \\ C_p - C_V &= \frac{p dV}{n dT} \\ &= \frac{p}{n} \cdot \frac{nR}{p} \\ &= R \\ C_p &= R + \frac{3}{2}R \\ &= \frac{5}{2}R \end{aligned}$$

## 19.2 Storing Energy in Bonds

- We know that

$$\begin{aligned}\frac{3}{2}kT &= \overline{KE}_{\text{molecule}} \\ &= \frac{1}{2}\mu\bar{v}^2 \\ &= \frac{1}{2}\mu\bar{v}_x^2 + \frac{1}{2}\mu\bar{v}_y^2 + \frac{1}{2}\mu\bar{v}_z^2\end{aligned}$$

- **Equipartition of energy theorem:** Every **degree of freedom** has associated with it, on average,  $\frac{1}{2}kT$  of energy.
  - Can be derived, but we're not expected to know this.
- **Degree of freedom:** Any direction that can be expressed as the time derivative of a coordinate, squared.
- For example, translational kinetic energy has three degrees of freedom:  $v_x^2$ ,  $v_y^2$ , and  $v_z^2$ .
  - Notice that since each has  $\frac{1}{2}kT$  of associated energy, the total translational kinetic energy has  $\frac{3}{2}kT$  of energy, as desired.
- Rotational kinetic energy has three degrees of freedom:

$$\begin{aligned}K_{\text{rot}} &= \frac{1}{2}I\omega^2 \\ &= \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2\end{aligned}$$

- For a diatomic molecule, it's symmetry implies that  $K_{\text{rot}}$  actually equals just  $\frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$ , if its axis is aligned with the  $x$ -axis.
- Thus, adding up these five degrees of freedom, we have that for each diatomic molecule,  $E_{\text{int}} = \frac{5}{2}kT$ .
  - This implies that for a mole of diatomic molecules,  $E_{\text{int}} = \frac{5}{2}RT$ , making  $C_V = \frac{5}{2}R$  and  $C_P = \frac{7}{2}R$ .
- Factoring in vibrational energy, if we let  $x$  be the separation between atoms, we have  $x^2$  and  $v_x^2$ , corresponding to potential- and kinetic-energy degrees of freedom.
  - This yields  $C_V = \frac{7}{2}R$  and  $C_P = \frac{9}{2}R$ .
- For hydrogen, we have changes in the molar heat capacity as a function of temperature.
  - This can be explained by the increase in degrees of freedom at higher temperatures (first only translational, then rotational gets added in, then vibrational).
  - Why? Quantum physics — more excited states become available at higher temperatures.
- If  $D$  is the number of degrees of freedom of a molecule, then

$$C_V = D \cdot \frac{1}{2}R$$

- On the other hand, it is always true that  $C_P = C_V + R$ .
- Similarly,  $E_{\text{int}} = D \cdot \frac{1}{2}nRT$ .

## 19.3 Thermal Expansion

- Consider a potential energy vs. bond stretch graph.
  - Since you can't push atoms too close together, the graph will be asymmetric.
  - Indeed, at higher energies, the bond will *stretch* more, but it will not shrink that much more.
  - Thus, the average separation increases, and the gas expands.
- **Coefficient of linear expansion:** The following quantity, where  $L$  is the length of something that's expanding.

$$\alpha = \frac{1}{L} \frac{dL}{dT}$$

- This formula essentially tells us how much something expands per unit increase in temperature:  
 $dL = \alpha L dT$ .
- If we have a circular metal disk with a hole, raising its temperature will enlarge the whole thing (both the outer radius and inner radius increase).