Lecture 2   The First Law of Thermodynamics (Ch.1)

Outline:

1. Internal Energy, Work, Heating
2. Energy Conservation – the First Law
3. Quasi-static processes
4. Enthalpy
5. Heat Capacity
The internal energy of a system of particles, \( U \), is the sum of the kinetic energy in the reference frame in which the center of mass is at rest and the potential energy arising from the forces of the particles on each other.

The internal energy is a state function – it depends only on the values of macroparameters (the state of a system), not on the method of preparation of this state (the “path” in the macroparameter space is irrelevant).

In equilibrium \([ f(P,V,T)=0 ]\): \( U = U(V, T) \)

\( U \) depends on the kinetic energy of particles in a system and an average inter-particle distance \( \sim V^{-1/3} \) – interactions.

For an ideal gas (no interactions): \( U = U(T) \) - “pure” kinetic
Internal Energy of an Ideal Gas

The internal energy of an ideal gas with \( f \) degrees of freedom:

\[
U = \frac{f}{2} N k_B T
\]

\( f \Rightarrow 3 \) (monatomic), 5 (diatomic), 6 (polyatomic)

(here we consider only trans.+rotat. degrees of freedom, and neglect the vibrational ones that can be excited at very high temperatures)

How does the internal energy of air in this (not-air-tight) room change with \( T \) if the external \( P = \text{const} \)?

\[
U = \frac{f}{2} N_{\text{in\_room}} k_B T = \left[ N_{\text{in\_room}} = \frac{PV}{k_B T} \right] = \frac{f}{2} PV
\]

- does not change at all, an increase of the kinetic energy of individual molecules with \( T \) is compensated by a decrease of their number.
We are often interested in $\Delta U$, not $U$. $\Delta U$ is due to:

- $Q$ - energy flow between a system and its environment due to $\Delta T$ across a boundary and a finite thermal conductivity of the boundary
  
  - heating ($Q > 0$) /cooling ($Q < 0$)
  
  (there is no such physical quantity as “heat”; to emphasize this fact, it is better to use the term “heating” rather than “heat”)

- $W$ - any other kind of energy transfer across boundary

Work and Heating are both defined to describe energy transfer across a system boundary.

Heating/cooling processes:

- **conduction**: the energy transfer by molecular contact – fast-moving molecules transfer energy to slow-moving molecules by collisions;
- **convection**: by macroscopic motion of gas or liquid
- **radiation**: by emission/absorption of electromagnetic radiation.
The First Law

The first law of thermodynamics: the internal energy of a system can be changed by doing work on it or by heating/cooling it.

\[ \Delta U = Q + W\]  

conservation of energy.

Sign convention: we consider \( Q \) and \( W \) to be positive if energy flows into the system.

For a cyclic process \( (U_i = U_f) \Rightarrow Q = -W \). If, in addition, \( Q = 0 \) then \( W = 0 \)

An equivalent formulation:

Perpetual motion machines of the first type do not exist.
Quasi-Static Processes

Quasi-static (quasi-equilibrium) processes – sufficiently slow processes, any intermediate state can be considered as an equilibrium state (the macroparameters are well-defined for all intermediate states).

**Advantage**: the state of a system that participates in a quasi-equilibrium process can be described with the same (small) number of macro parameters as for a system in equilibrium (e.g., for an ideal gas in quasi-equilibrium processes, this could be $T$ and $P$). By contrast, for non-equilibrium processes (e.g. turbulent flow of gas), we need a huge number of macro parameters.

**Examples of quasi-equilibrium processes:**
- isochoric: $V = \text{const}$
- isobaric: $P = \text{const}$
- isothermal: $T = \text{const}$
- adiabatic: $Q = 0$

For quasi-equilibrium processes, $P$, $V$, $T$ are well-defined – the “path” between two states is a continuous lines in the $P$, $V$, $T$ space.
The work done by an external force on a gas enclosed within a cylinder fitted with a piston:

\[ W = (PA) \, dx = P (Adx) = - PdV \]

force

The sign: if the volume is decreased, \( W \) is positive (by compressing gas, we increase its internal energy); if the volume is increased, \( W \) is negative (the gas decreases its internal energy by doing some work on the environment).

\[ W_{1-2} = -\int_{V_1}^{V_2} P(T,V) \, dV \]

\[ dU = Q - PdV \]

The work is not necessarily associated with the volume changes – e.g., in the Joule’s experiments on determining the “mechanical equivalent of heat”, the system (water) was heated by stirring.
$W_{1-2} = -\int_{V_1}^{V_2} P(T,V) dV$

- we can bring the system from state 1 to state 2 along infinite # of paths, and for each path $P(T,V)$ will be different.

Since the work done on a system depends not only on the initial and final states, but also on the intermediate states, it is not a state function.

$\Delta U = Q + W$  

$U$ is a state function, $W$ - is not $\Rightarrow$ thus, $Q$ is not a state function either.

$W_{net} = W_{AB} + W_{CD} = -P_2(V_2-V_1) - P_1(V_1-V_2)$

$= -(P_2-P_1)(V_2-V_1) < 0$

- the work is negative for the “clockwise” cycle; if the cyclic process were carried out in the reverse order (counterclockwise), the net work done on the gas would be positive.
Comment on State Functions

$U$, $P$, $T$, and $V$ are the state functions, $Q$ and $W$ are not. Specifying an initial and final states of a system does not fix the values of $Q$ and $W$, we need to know the whole process (the intermediate states). Analogy: in classical mechanics, if a force is not conservative (e.g., friction), the initial and final positions do not determine the work, the entire path must be specified.

In math terms, $Q$ and $W$ are not exact differentials of some functions of macroparameters. To emphasize that $W$ and $Q$ are NOT the state functions, we will use sometimes the curled symbols $\delta$ (instead of $d$) for their increments ($\delta Q$ and $\delta W$).

\[
d U = T d S - P dV \quad - \text{an exact differential}
\]

\[
d z = A_x(x, y) dx + A_y(x, y) dy \quad - \text{it is an exact differential if it is the difference between the values of some (state) function $z(x, y)$ at these points:}
\]

\[
d z = z(x + dx, y + dy) - z(x, y)
\]

A necessary and sufficient condition for this:

\[
A_x(x, y) = \frac{\partial z(x, y)}{\partial x} \quad A_y(x, y) = \frac{\partial z(x, y)}{\partial y}
\]

If this condition holds:

\[
\frac{\partial A_x(x, y)}{\partial y} = \frac{\partial A_y(x, y)}{\partial x}
\]

\[
d z = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy
\]

e.g., for an ideal gas:

\[
\delta Q = dU + PdV = Nk_B \left(\frac{f}{2} dT + \frac{T}{V} dV\right) \quad - \text{cross derivatives are not equal}
\]
Imagine that an ideal monatomic gas is taken from its initial state \( A \) to state \( B \) by an *isothermal* process, from \( B \) to \( C \) by an *isobaric* process, and from \( C \) back to its initial state \( A \) by an *isochoric* process. Fill in the signs of \( Q \), \( W \), and \( \Delta U \) for each step.

\[
U = \frac{f}{2} N k_B T \quad PV = N k_B T
\]
Quasistatic Processes in an Ideal Gas

**Isochoric** \((V = \text{const})\)

\[ W_{1 \rightarrow 2} = 0 \]

\[ Q_{1 \rightarrow 2} = \frac{3}{2} N k_B (T_2 - T_1) > 0 \quad (= C_v \Delta T) \]

\( \text{(see the last slide)} \)

\[ dU = Q_{1 \rightarrow 2} \]

**Isobaric** \((P = \text{const})\)

\[ W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} P(V,T) dV = - P (V_2 - V_1) < 0 \]

\[ Q_{1 \rightarrow 2} = \frac{5}{2} N k_B (T_2 - T_1) > 0 \quad (= C_p \Delta T) \]

\[ dU = W_{1 \rightarrow 2} + Q_{1 \rightarrow 2} \]
Isothermal Process in an Ideal Gas

\[ PV = Nk_B T \]

\[ W_{i-f} = Nk_B T \ln \frac{V_i}{V_f} \]

\( W_{i-f} > 0 \) if \( V_i > V_f \) (compression)

\( W_{i-f} < 0 \) if \( V_i < V_f \) (expansion)

Isothermal (\( T = \text{const} \)):

\[ dU = 0 \]

\[ W_{1 \rightarrow 2} = -\int_{V_1}^{V_2} P(V,T) dV = -Nk_B T \int_{V_1}^{V_2} \frac{dV}{V} = -Nk_B T \ln \frac{V_2}{V_1} \]

\[ Q_{1 \rightarrow 2} = -W_{1 \rightarrow 2} \]
Adiabatic Process in an Ideal Gas

An adiabatic (thermally isolated) system

\( Q_{1 \rightarrow 2} = 0 \quad dU = W_{1 \rightarrow 2} \)

The amount of work needed to change the state of a thermally isolated system depends **only** on the initial and final states and not on the intermediate states.

\[
W_{1 \rightarrow 2} = -\int_{V_i}^{V_2} P(V,T) dV
\]

To calculate \( W_{1-2} \), we need to know \( P(V,T) \) for an adiabatic process

\[
U = \frac{f}{2} Nk_B T \quad \Rightarrow \quad dU = \frac{f}{2} Nk_B dT = -PdV
\]

(\( f \) – the # of “unfrozen” degrees of freedom)

\[
PV = Nk_B T \quad \Rightarrow \quad PdV + VdP = Nk_B dT \quad \Rightarrow \quad PdV + VdP = -\frac{2}{f} PdV \quad \bigg| \div PV
\]

\[
\frac{dV}{V} \left(1 + \frac{2}{f}\right) + \frac{dP}{P} = 0 \quad \int, \quad \gamma = 1 + \frac{2}{f} \quad \text{Adiabatic exponent}
\]

\[
\gamma \int_{V_i}^{V} \frac{dV}{V} + \int_{P_i}^{P} \frac{dP}{P} = 0
\]

\[
\ln \left( \frac{V}{V_1} \right)^\gamma = \ln \left( \frac{P_1}{P} \right) \quad \Rightarrow \quad PV^\gamma = P_1V_1^\gamma = \text{const}
\]
An adiabata is “steeper” than an isotherma: in an adiabatic process, the work flowing out of the gas comes at the expense of its thermal energy ⇒ its temperature will decrease.

\[ PV^\gamma = P_1V_1^\gamma = \text{const} \]

\[ W_{1\rightarrow 2} = -\int_{V_1}^{V_2} P(V, T)dV = -\int_{V_1}^{V_2} \frac{P_1V_1^\gamma}{V^\gamma} dV = -P_1V_1^\gamma \frac{1}{-\gamma + 1} \left. V^{-\gamma+1} \right|_{V_1}^{V_2} \]

\[ \gamma \Rightarrow 1+2/3 \approx 1.67 \text{ (monatomic), } 1+2/5 = 1.4 \text{ (diatomic), } 1+2/6 \approx 1.33 \text{ (polyatomic) } \]

(again, neglecting the vibrational degrees of freedom)

Prove \[ W_{1\rightarrow 2} = \frac{f}{2} \Delta(PV) = \frac{f}{2} Nk_B \Delta T = \Delta U \]
## Summary of quasi-static processes of ideal gas

\[ \Delta U \equiv U_f - U_i \]

<table>
<thead>
<tr>
<th>Quasi-Static process</th>
<th>( \Delta U )</th>
<th>( Q )</th>
<th>( W )</th>
<th>Ideal gas law</th>
</tr>
</thead>
<tbody>
<tr>
<td>isobaric (( \Delta P = 0 ))</td>
<td>[ \Delta U = \frac{f}{2} Nk_B \Delta T = \frac{f}{2} P \Delta V ]</td>
<td>( \frac{f}{2} P \Delta V )</td>
<td>( -P \Delta V )</td>
<td>( \frac{V_i}{T_i} = \frac{V_f}{T_f} )</td>
</tr>
<tr>
<td>isochoric (( \Delta V = 0 ))</td>
<td>[ \Delta U = \frac{f}{2} Nk_B \Delta T = \frac{f}{2} (\Delta P)V ]</td>
<td>( \frac{f}{2} (\Delta P)V )</td>
<td>0</td>
<td>( \frac{P_i}{T_i} = \frac{P_f}{T_f} )</td>
</tr>
<tr>
<td>isothermal (( \Delta T = 0 ))</td>
<td>0</td>
<td>( -W )</td>
<td>( -Nk_B T \ln \frac{V_f}{V_i} )</td>
<td>( PV_i = P_f V_f )</td>
</tr>
<tr>
<td>adiabatic (( Q = 0 ))</td>
<td>[ \Delta U = \frac{f}{2} Nk_B \Delta T = \frac{f}{2} \Delta(PV) ]</td>
<td>0</td>
<td>( \Delta U )</td>
<td>( P V_i^{\gamma} = P_f V_f^{\gamma} )</td>
</tr>
</tbody>
</table>
Problem

Imagine that we rapidly compress a sample of air whose initial pressure is $10^5 \text{ Pa}$ and temperature is $22^\circ \text{C} (= 295 \text{ K})$ to a volume that is a quarter of its original volume (e.g., pumping bike’s tire). What is its final temperature?

Rapid compression – approx. adiabatic, no time for the energy exchange with the environment due to thermal conductivity

$$
\begin{align*}
PV_1 &= Nk_B T_1 \\
P_2 V_2 &= Nk_B T_2 \\
PV_1^\gamma &= P_2 V_2^\gamma
\end{align*}
\right\}
\Rightarrow P_2 = \frac{PV_1^\gamma}{V_2^\gamma} = \frac{PV_1^\gamma}{V_2^\gamma} = Nk_B T_2 = \frac{PV_1}{T_1} T_2 \Rightarrow \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1}
$$

For adiabatic processes:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = \text{const}$$

also

$$P^{\gamma-1} / T^\gamma = \text{const}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} = 295 \text{ K} \times 4^{0.4} \approx 295 \text{ K} \times 1.74 \approx 514 \text{ K}$$

- poor approx. for a bike pump, works better for diesel engines
Non-equilibrium Adiabatic Processes

Free expansion

1. \( TV^{\gamma-1} = \text{const} \)  
   \( V \) – increases  
   \( \Rightarrow T \) – decreases (cooling)

2. On the other hand, \( \Delta U = Q + W = 0 \)  
   \( U \sim T \Rightarrow T \) – unchanged  
   (agrees with experimental finding)

Contradiction – because approach #1 cannot be justified – violent expansion of gas is not a quasi-static process. \( T \) must remain the same.

\[ TV^{\gamma-1} = \text{const} \]
- applies only to quasi-equilibrium processes !!!
The Enthalpy

Isobaric processes (\(P = \text{const}\)):

\[
dU = Q - P\Delta V = Q - \Delta(PV) \Rightarrow Q = \Delta U + \Delta(PV)
\]

\[
\Rightarrow H \equiv U + PV - \text{the enthalpy}
\]

The enthalpy is a \textit{state function}, because \(U\), \(P\), and \(V\) are state functions. In isobaric processes, the energy received by a system by heating equals to the change in enthalpy.

\[
\begin{align*}
\text{isochoric:} & \quad Q = \Delta U \\
\text{isobaric:} & \quad Q = \Delta H
\end{align*}
\]

\(\text{in both cases, } Q \text{ does not depend on the path from 1 to 2.}\)

\textbf{Consequence:} the energy released (absorbed) in chemical reactions at constant volume (pressure) depends only on the initial and final states of a system.

\textbf{The enthalpy of an ideal gas:} \( H = U + PV = \frac{f}{2} Nk_B T + Nk_B T = \left(\frac{f}{2} + 1\right) Nk_B T \) (depends on \(T\) only)
The heat capacity of a system - the amount of energy transfer due to heating required to produce a unit temperature rise in that system

\[ C \equiv \frac{\delta Q}{\Delta T} \]

\( C \) is NOT a state function (since \( Q \) is not a state function) – it depends on the path between two states of a system \( \Rightarrow \)

( isothermic – \( C = \infty \), adiabatic – \( C = 0 \))

The specific heat capacity \( c \equiv \frac{C}{m} \)
To find $C_P$ and $C_V$, we need $f(P,V,T) = 0$ and $U = U(V,T)$.

**For an ideal gas**

- $U = \frac{f}{2} N k_B T$
- $H = \left(\frac{f}{2} + 1\right) N k_B T$

$$C_V = \frac{f}{2} N k_B = \frac{f}{2} n R$$

$$C_P = \left(\frac{f}{2} + 1\right) n R$$

For one mole of a monatomic ideal gas:

$$C_V = \frac{3}{2} R \quad C_P = \frac{5}{2} R$$
Another Problem

During the ascent of a meteorological helium-gas filled balloon, its volume increases from $V_i = 1 \text{ m}^3$ to $V_f = 1.8 \text{ m}^3$, and the pressure inside the balloon decreases from 1 bar ($=10^5 \text{ N/m}^2$) to 0.5 bar. Assume that the pressure changes linearly with volume between $V_i$ and $V_f$.

(a) If the initial $T$ is 300K, what is the final $T$?

(b) How much work is done by the gas in the balloon?

(c) How much “heat” does the gas absorb, if any?

\[
P(V) = -0.625 \text{ bar/m}^3 \times V + 1.625 \text{ bar}
\]

\[
(a) \quad PV = Nk_B T \quad T = \frac{PV}{Nk_B} \quad T_f = T_i \frac{P_f V_f}{P_i V_i} = 300 \text{K} \frac{0.5 \text{ bar} \times 1.8 \text{ m}^3}{1 \text{ bar} \times 1 \text{ m}^3} = 270 \text{K}
\]

(b) $\delta W_{ON} = - \int_{V_i}^{V_f} P(V) dV$ - work done on a system $\delta W_{BY} = \int_{V_i}^{V_f} P(V) dV$ - work done by a system

\[
\delta W_{ON} = - \delta W_{BY} \quad \delta W_{BY} = \int_{V_i}^{V_f} P(V) dV = \left(0.5 \times 0.8 \text{ bar} \cdot \text{m}^3 + 0.5 \times 0.4 \text{ bar} \cdot \text{m}^3\right) = 0.6 \text{ bar} \cdot \text{m}^3 = 6 \times 10^4 \text{ J}
\]

(c) $\Delta U = \delta Q + \delta W_{ON}$

\[
\delta Q = \Delta U - \delta W_{ON} = \frac{3}{2} Nk_B \left(T_f - T_i\right) - W_{ON} = \frac{3}{2} P_i V_i \left(\frac{T_f}{T_i} - 1\right) + \delta W_{BY} = 1.5 \times 10^5 \text{J} \times (-0.1) + 6 \times 10^4 \text{J} = 4.5 \times 10^4 \text{J}
\]