

Lecture 38

First law of thermodynamics.

Internal energy

State variables: p, T, V

They only depend on the "state" of the system

They do NOT depend on the "history"

Total energy of the molecules is **also a state variable**:

Internal energy: $U = KE_{\text{all}} + PE_{\text{all}}$

KE : kinetic energy of atoms, random motion

PE : interactions, e.g. attraction between molecules

Internal energy of an ideal gas

Monoatomic ideal gas: $U = KE_{\text{all}} = N \left(\frac{3}{2} kT \right) \xrightarrow{Nk = nN_A k = nR} U = \frac{3}{2} nRT$

In an ideal gas, the internal energy only depends on temperature.

In general, it may depend on volume, etc (but never on history)

Beyond the monoatomic ideal gas

Until now, this microscopic model is only valid for monoatomic molecules.

Monoatomic molecules (points) have 3 degrees of freedom (translational)

Diatomic molecules (points) have 5 degrees of freedom: 3 translational + 2 rotational

Principle of equipartition of energy: each velocity component (radial or angular) has, on average, associated energy of $\frac{1}{2} kT$

The equipartition principle is very general.

Diatomic ideal gas

$$\begin{aligned} \langle KE \rangle &= \langle KE_{tr} \rangle + \langle KE_{rot} \rangle \\ &= \frac{3}{2}kT + \frac{2}{2}kT \\ &= \frac{5}{2}kT \end{aligned}$$

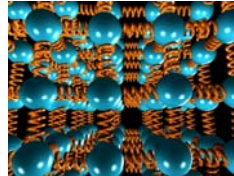
Average energy per molecule

The same temperature involves more energy per molecule for a diatomic gas than for a monoatomic gas..

Average total energy: $U = \frac{5}{2}NkT = \frac{5}{2}nRT$

Monoatomic solid

Simple model of a solid crystal: atoms held together by springs.



$$\langle KE_i \rangle = \frac{3}{2}kT \quad \text{Vibrations in 3 directions}$$

But we also have potential energy!

$$\langle PE_i \rangle = \langle KE_i \rangle \quad (\text{for any harmonic oscillator})$$

For N atoms:

$$U = N \langle KE_i \rangle + N \langle PE_i \rangle = 2N \langle KE_i \rangle$$

$$U = 3NkT = 3nRT$$

Changes in internal energy

Temperature change is associated to heat transfer.

Change in internal energy

transfer of energy

We already know that:

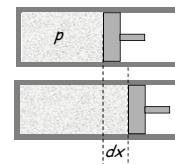
When heat is absorbed/released by a system, its internal energy increases/decreases.

Other ways of transferring energy?

Work!!

Work done by gas volume change

A gas with pressure p expands by pushing a piston by a distance dx



Force by gas on piston $F = pA$
(A = area of the piston)

Work by gas: $dW = pAdx = pdV$

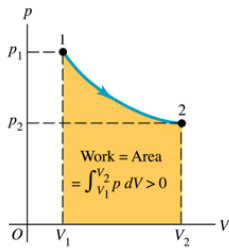
As volume goes from V_i to V_f

$$W = \int_{V_i}^{V_f} pdV$$

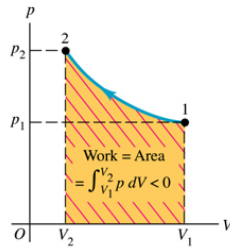
Work is the area under pV curve

But be careful with the sign!

Expansion
(Work done by gas) > 0

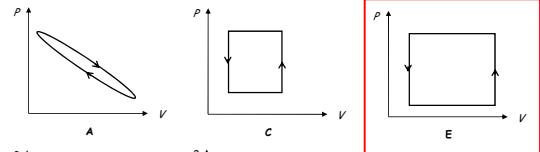


Compression
(Work done by gas) < 0



In-class example: Work in closed cycle

Which of these processes represents the most work done by the system per cycle?



Work = area inside cycle.

Note that $W_E < 0$

CW $\Leftrightarrow W > 0$

CCW $\Leftrightarrow W < 0$

First law of thermodynamics

If heat is absorbed by a system, $Q > 0$ $\Delta U > 0$

If heat is released by a system, $Q < 0$ $\Delta U < 0$

If work is done by the gas (expansion), $W > 0$ $\Delta U < 0$

If work is done on the gas (compression), $W < 0$ $\Delta U > 0$

$$\Delta U = Q - W$$

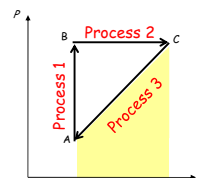
Remember the sign convention!

$W > 0$ work done by system

$Q > 0$ heat absorbed by system

Example: Cyclic process

A gas (not necessarily ideal) goes through the cycle shown in the pV diagram below.



Data: $V_A = 2.0 \text{ m}^3$ $P_A = 1.0 \times 10^5 \text{ Pa}$
 $V_C = 4.0 \text{ m}^3$ $P_C = 2.0 \times 10^5 \text{ Pa}$

a) Determine the work done by the gas in each of the three parts of the cycle.

1 (A to B): $W_1 = 0$ (constant volume)

2 (B to C): $W_2 = p\Delta V = p_B(V_C - V_B) = 2 \times 10^5 \text{ J}$

3 (C to A): $W_3 = -(\text{yellow area}) = -3 \times 10^5 \text{ J}$

Data: $V_A = 2.0 \text{ m}^3$ $P_A = 1.0 \times 10^5 \text{ Pa}$
 $V_C = 4.0 \text{ m}^3$ $P_C = 2.0 \times 10^5 \text{ Pa}$

b) For the entire cycle, what are the work done by the gas, the change in internal energy of the gas and the heat exchanged with the surroundings? Is this heat absorbed or released by the gas?

$$W_{\text{cycle}} = W_1 + W_2 + W_3 = -1 \times 10^5 \text{ J}$$

$$\Delta U_{\text{cycle}} = U_f - U_i = U_A - U_A = 0 \quad \longrightarrow \quad \Delta U_{\text{closed cycle}} = 0$$

$$Q_{\text{cycle}} = \Delta U_{\text{cycle}} + W_{\text{cycle}} = -1 \times 10^5 \text{ J}$$

$Q < 0$: heat is released by the gas

Overall, in this cycle:

$W_{\text{cycle}} < 0$ Work done on the system.
 $Q_{\text{cycle}} < 0$ System releases heat.

We do work on the system, we obtain heat.
 (This could be used to warm up a room...)

Reverse cycle (A → C → B):

$W_{\text{cycle}} > 0$ Work done by the system.
 $Q_{\text{cycle}} > 0$ System absorbs heat.

System absorbs heat and produces work.
 (Like some kind of steam motor...)