

## WORK ON A GAS: $W = -p\Delta V$ .

In  $pV$  space the work done by an expanding gas is the area under the  $pV$  curve. It is often easy to estimate this using elementary ideas of area.

## FIRST LAW OF THERMODYNAMICS:

$$\Delta U = Q + W.$$



It's assumed in choosing signs that  $Q$  and  $W$  are input to the gas.

**EQUIPARTITION THEOREM:** Each degree of freedom contributes  $(1/2)k_B T$ .

## THERMAL PROCESSES:

- ISOBARIC ( $\Delta p = 0$ )
- ADIABATIC (no added  $Q$ )
- ISOVOLUMETRIC ( $\Delta V = 0$ )
- ISOTHERMAL ( $\Delta T = \Delta U = 0$ ).

# THERMAL PROCESSES:

We always picture these undergone by a gas so that we can use the ideal gas law,  $pV = Nk_B T$ , as the equation of state. For other systems, we would need to know and use the equation of state for those systems.

• **Isobaric Processes:** In such processes the pressure of the gas,  $p$ , is held constant. Since  $\Delta p = 0$ , the work done by a gas, for example, is  $\Delta W = -p\Delta V$ , and is thus easy to calculate without using calculus. Since an expanding gas would cool, its pressure would be expected to decrease, so the only way to have such a process is to add heat while it is going on. Using  $\Delta U = Q + W$ , we get  $Q = \Delta U + p\Delta V$ . The ideal gas law would then give  $Q = nC_p\Delta T$  where  $C_p = (5/2)R = C_v + R$ .

• **Adiabatic Processes:** In such processes, no heat is added to or leaves the system. [Many processes in the earth's atmosphere are adiabatic, as are processes that occur in piston heat engines like the automobile engine.] Therefore we would have  $\Delta U = W$ . You can find the area under the  $pV$  curve for such a process using calculus and one of the im-

portant results is that for adiabatic processes,

$$pV^\gamma = \text{const.},$$

where  $\gamma = C_p/C_v$ , which is about 1.66 for monatomic gases.

• **Isovolumetric Processes:** If  $\Delta V = 0$ , clearly, the gas can't do work, so  $W = 0$  and  $\Delta U = Q$ . Furthermore  $Q = nC_v\Delta T$ , based on the Ideal Gas Law.

• **Isothermal Processes:** If  $\Delta T = 0$  then for an ideal gas,  $\Delta U = 0$ . Therefore from conservation of energy,  $W = -Q$ . The gas law then requires  $p \propto V^{-1}$ , as a gas expands. Using calculus you can get the work done on the gas (the area under the  $pV$  curve), and it is found to be

$$W = -nRT \ln \left[ \frac{V_f}{V_i} \right].$$

Inclusive example: We have  $0.03 \text{ m}^3$  of a monatomic ideal gas at an initial temperature of  $310 \text{ K}$ , and a pressure of  $1.5 \times 10^5 \text{ J/m}^3$ . (a) How many moles of the gas are present? (b) If the gas is heated at constant pressure to twice the original volume, what is its new temperature? (c) Instead, the gas undergoes an isothermal expansion to twice its original volume. What is its new pressure? How much work did the gas do? (d) Instead, the gas undergoes an adiabatic expansion to twice its original volume. What are its new temperature and pressure? (e) Instead, the gas undergoes an isovolumetric process to a new pressure 2 times its original pressure. What is the final temperature of the gas?

## HEAT ENGINES:

Consider a single cycle in which  $Q_H$  is drawn from a reservoir at  $T_H$ ,  $Q_C$  is exhausted to a reservoir at  $T_C$ , and work  $W_e$  is done.

$$\Delta U = 0 = Q + W = (Q_H - Q_C) - W_e.$$

Therefore  $W_e = Q_H - Q_C$ . Define efficiency

$$\epsilon = W_e/Q_H = 1 - (Q_C/Q_H).$$

For heat pumps, which are engines run in reverse,  $\text{COP} = Q_C/W$  so  $\text{COP} = 1/((Q_H/Q_C) - 1)$ .

## 2nd Law of Thermodynamics

$\Delta S = Q/T \geq 0$  for any process in nature.

The entropy  $S$  is defined microscopically as  $k_B \ln N_{ms}$ .

This explains why the efficiency of engines is so far from 100%. Imagine an impossible  $\Delta S = 0$  process.

Then  $(Q_C/T_C) - (Q_H/T_H) = 0$ , and therefore  $\epsilon_C = 1 - (T_C/T_H)$ .

For most processes  $\epsilon \simeq \epsilon_C/2$ .

## Different Statements of the 2nd Law:

- No process can convert 100% of a heat flow into work. [  $\epsilon \ll 100\%$  ]
- In a closed system, any  $\Delta T$  will eventually go to zero. [“Heat Death”]
- A system will wind up in more and more probable states as time goes by, unless it starts in a most probable state.
- All energy releases are eventually entirely dissipated as heat.
- All basic processes involving complex systems are irreversible. [“Time’s Arrow”] This does not necessarily apply to processes involving fundamental point particles.

Statistical Entropy  $S = k_B \ln N_{ms}$ .

Thermodynamic Entropy  $\Delta S = Q/T$ .

Show that heat only flows from higher  $T$  regions to lower  $T$  regions because this is the direction that results in  $\Delta S > 0$ .

Show that an engine in one cycle cannot convert a flow of heat entirely into work, because this would result in  $\Delta S < 0$ .

In one cycle of an engine, 1000 J are extracted from a 400 K region and 800 J are dumped into a 300 K region. What is  $\Delta S$  per cycle?

1 kg of ice melts to 1 kg of liquid water without temperature change. What is  $\Delta S$ ?

If the room in which the ice in the previous question is melting is at 300 K, what is the total entropy change of the world as the ice melts?

Statistical Entropy  $S = k_B \ln N_{ms}$ .

Thermodynamic Entropy  $\Delta S = Q/T$ .