

OVERVIEW

- Equations of state
- State diagrams and thermodynamic processes
- Work and heat
- First law of thermodynamics

EQUATIONS OF STATE

Consider a chunk of material in equilibrium with its environment.

environment T_E

system $T_S = T_E$

temperature T , pressure p , volume V

mass m

(equivalently, number of moles $\nu = m/\mu$)

...

State variables: Observable, measurable quantities which characterize the state of a material.

State variables are not independent of each other.

\Rightarrow *Equation of state:*

$$f(p, V, T, \nu) = 0$$

EQUATIONS OF STATE (EoS)

EoS are different for different materials.

Q: Where do we get them from?

A: It depends

It does not need to be an equation really. Can be a numerical table, for example. Or a computer program.

- Microscopic way: Derive from a microscopic model of a material. (if we can)
- Empirical way: Construct an approximate eq. of state using measurable phenomenological quantities.

EQUATIONS OF STATE: EXAMPLES

Example: a phenomenological EoS of a solid.

Let the the volume of a sample is V_0 at temperature T_0 and pressure p_0 . Then, using

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (\text{volume expansion coefficient})$$

and

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (\text{compressibility})$$

$$V = V_0 [1 + \beta(T - T_0) - \kappa(p - p_0)]$$

(Only valid for $|T - T_0| \ll T_0$, $|p - p_0| \ll p_0$ and $|V - V_0| \ll V_0$)

EQUATIONS OF STATE: IDEAL GAS

Ideal gas equation:

$$pV = \nu RT$$

where $R = 8.31 \text{ J/mol}\cdot\text{K}$ is the *ideal gas constant*.

- Works extremely well around room temperature and atmospheric pressure
- Can actually be derived microscopically
- Will discuss in greater detail later on. For now, just take this equation as an experimental fact.

EQUATIONS OF STATE: VAN DER WAALS EQUATION

One possible way of correcting the ideal gas law: *van der Waals equation*

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

(for simplicity, I put $\nu = 1$.)

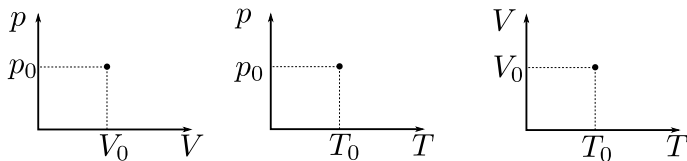
Here a and b are phenomenological constants, which are different for different gases.

vdW equation can describe liquid-gas transitions (which an ideal gas model cannot). Will discuss later on.

STATE DIAGRAMS AND THERMODYNAMIC PROCESSES

Consider ν moles of substance with EoS $f(p, T, V) = 0$.
Suppose it occupies the volume V_0 and has the temperature T_0 .
Its pressure p_0 is then a solution of $f(p_0, T_0, V_0) = 0$.

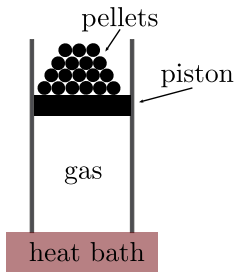
Given a pair of state variables T_0 and V_0 , we depict the state of the system by a point on the T - V plane.



Notice: all three plots show *the same* state!

QUASI-EQUILIBRIUM PROCESSES

Consider a specific thermodynamic system: a vessel of gas (not necessarily ideal).

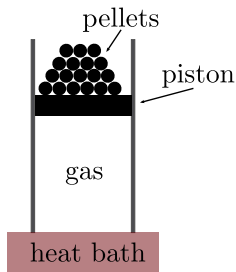


The vessel is in contact with the heat bath, the temperature of the latter can be controlled externally. The piston is frictionless, and its mass can be controlled by adding/removing lead pellets.

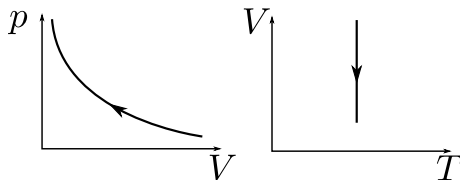
Add a few pellets, let the gas re-equilibrate, repeat \Rightarrow a *quasi-equilibrium* compression.

(Meaning: at every point in time the gas is approximately in a thermal equilibrium.)

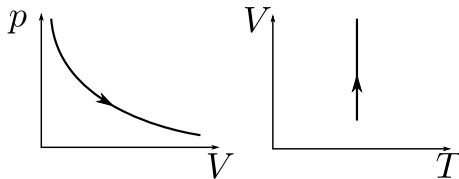
ISOTHERMAL COMPRESSION AND EXPANSION



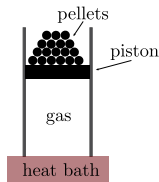
Keep adding pellets slowly, but keep the heat bath's T fixed. The T of the gas is fixed, but the volume shrinks: it's *isothermal* compression.



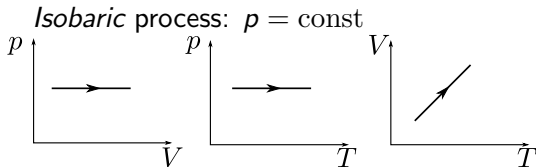
A reverse process: remove pellets one by one. It's *isothermal expansion*



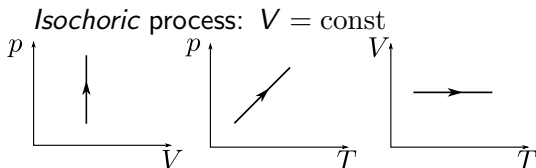
ISOBARIC AND ISOCHORIC PROCESSES



Keep the weight of the piston fixed, and increase the temperature: it's *isobaric* expansion

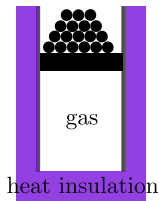


NB: the exact shape of the T - V path depends on the EoS



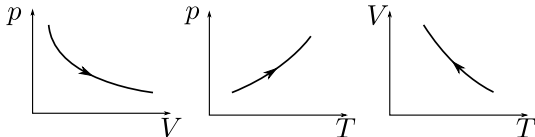
NB: the exact shape of the T - p path depends on the EoS

ADIABATIC PROCESS



Remove the heat bath and wrap the vessel by a heat insulator: no heat transfer in or out of the vessel \Rightarrow *adiabatic* process.

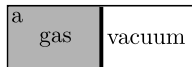
Adiabatic process: no heat exchange with the environment



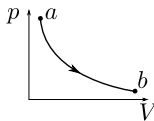
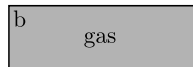
NB: the exact shapes of the all the curves depend on the EoS

REVERSIBLE AND IRREVERSIBLE PROCESSES

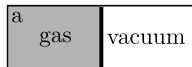
REVERSIBLE EXPANSION:



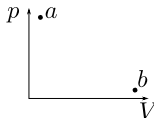
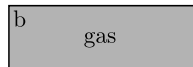
→ slowly move the partition →



IRREVERSIBLE EXPANSION:



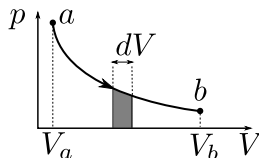
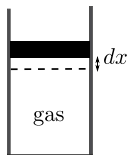
→ break the partition →



Intermediate states cannot be drawn on the p - V diagram!

WORK DONE IN A THERMODYNAMIC PROCESS

Suppose the gas expands so that the piston moves upwards by dx



Work done by the gas is

$$\delta W = F dx = (pA) dx = p(A dx) = p dV$$

so that the net work done from a to b is

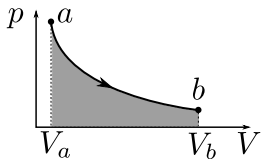
$$W = \int_{V_a}^{V_b} p dV$$

WORK DONE IN A THERMODYNAMIC PROCESS

SIGN CONVENTION:

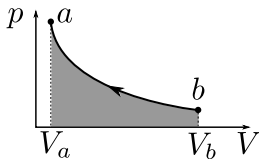
In thermodynamics, W is always the work done *by* the system, not work done *on* the system.

Expansion:



$$W_{a \rightarrow b} = \int_{V_a}^{V_b} p dV > 0$$

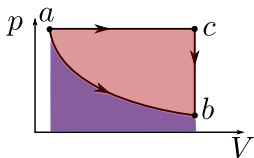
Compression:



$$\begin{aligned} W_{b \rightarrow a} &= \int_{V_b}^{V_a} p dV \\ &= - \int_{V_a}^{V_b} p dV < 0 \end{aligned}$$

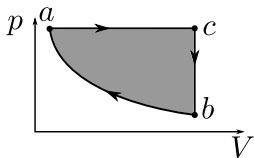
WORK DONE IN A THERMODYNAMIC PROCESS

Work done while going from a to b is path-dependent:



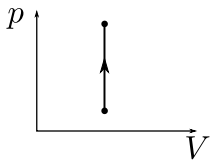
$$W_{a \rightarrow b \rightarrow c} > W_{a \rightarrow b}$$

Moreover, net work done in a closed path is not zero:



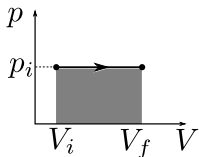
$$W_{a \rightarrow c \rightarrow b \rightarrow a} = W_{a \rightarrow c} - W_{a \rightarrow b}$$

EXAMPLES:



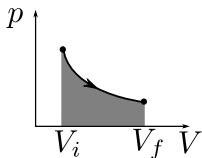
Isochoric process, $V = \text{const}$

$$W = 0$$



Isobaric process, $p = \text{const}$

$$W = \int_{V_i}^{V_f} p \, dV = p_i(V_f - V_i)$$



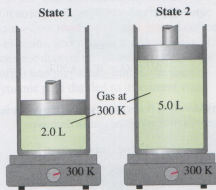
Isothermal process, $T = \text{const}$, ideal gas *only*

$$pV = \nu RT \Rightarrow p = \nu RT/V$$

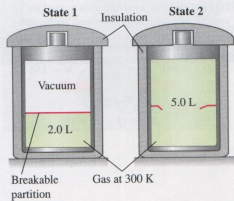
$$W = \int_{V_i}^{V_f} p \, dV = \int_{V_i}^{V_f} \nu RT \frac{dV}{V} = \nu RT \log \frac{V_f}{V_i}$$

HEAT ADDED IN A THERMODYNAMIC PROCESS

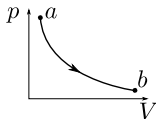
(a) System does work on piston; hot plate adds heat to system ($W > 0$ and $Q > 0$).



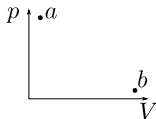
(b) System does no work; no heat enters or leaves system ($W = 0$ and $Q = 0$).



Reversible expansion: $W > 0$, $Q > 0$



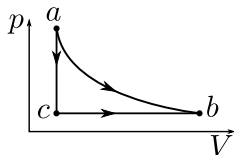
Irreversible expansion: $W = 0$, $Q = 0$



The initial and final states are the same. Both work done *and* heat added depend on the process.

HEAT ADDED IN A THERMODYNAMIC PROCESS

For reversible expansions, both heat and work are path dependent as well.



If $a \rightarrow b$ is adiabatic, $Q_{a \rightarrow b} = 0$

But $Q_{a \rightarrow c \rightarrow b} \neq 0$

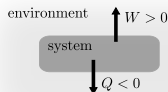
EXPERIMENTAL FACT:

the difference between heat added to the system and work done by the system *only* depends on the final and initial states:

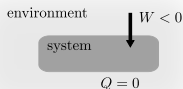
Q	depends on the path,	W	depends on the path,
$W + Q$	depends on the path,	$W - 2Q$	depends on the path,
$W - Q$	<i>does not</i>		

FIRST LAW OF THERMODYNAMICS

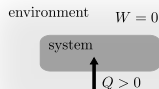
The change of *internal energy* $\Delta U = Q - W$



$$\Delta U = Q - W < 0$$



$$\Delta U = Q - W > 0$$



$$\Delta U = Q - W > 0$$

FIRST LAW OF THERMODYNAMICS: $Q = \Delta U + W$

The (energy added as) heat equals the change of internal energy of the system plus work (done by the system)

...which is just conservation of energy

INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

- Microscopically, internal energy is the sum of kinetic energies of molecules and potential energies of their interactions with each other
- Internal energy is defined for a *state of a system*, unlike heat and work, which are only defined for a *path*:

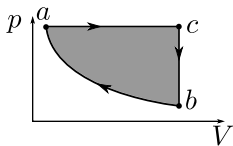
$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

- When we talk about *internal* energy, we mean it's defined in the reference frame where the system as a whole is at rest. The kinetic energy of the motion of the center of mass of the system is extra.

For example: the total energy of a mole of air is the sum of the kinetic energy of the center-of-mass motion (related to the wind velocity) and the internal energy (related to the temperature)

EXAMPLES: CYCLIC PROCESSES AND ISOLATED SYSTEMS

- For any *cyclic process*, where the system returns to its initial state,



$$Q \neq 0 \quad W \neq 0$$

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = 0 \quad \Rightarrow \quad Q = W$$

- An *isolated system*: no heat flow in or out, no work done:

$$Q = W = 0 \quad \Rightarrow \quad \Delta U = 0$$

Which means that $U_{\text{final}} = U_{\text{initial}}$: *internal energy of an isolated system remains constant in time.*

FIRST LAW OF THERMODYNAMICS

For infinitesimal changes of state ($T \rightarrow T + dT$ and/or $V \rightarrow V + dV$ and/or $p \rightarrow p + dp$) the first law of thermodynamics reads

$$\delta Q = dU + \delta W$$

δQ and δW are the so-called *inexact differentials*:

$U = U(T, V)$ is a well-defined function of state,

$$\begin{aligned} dU &= U(T + dT, V + dV) - U(T, V) \\ &= \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV, \end{aligned}$$

irrespective of the path between (T, V) and $(T + dT, V + dV)$.

For δQ and δW such expressions *do not exist*

HEAT CAPACITIES

Add δQ of heat to the system. The temperature changes by dT .
The heat capacity is then

$$C = \frac{\delta Q}{dT} \quad (\text{which depends on } \textit{how} \text{ the heat is added})$$

ISOCHORIC HEAT CAPACITY ($V = \text{const}$):

$$\delta Q = C_V dT$$

The first law of thermodynamics ($dW = p dV = 0$):

$$\delta Q = dU \quad \Rightarrow \quad dU = C_V dT$$

If $C_V = \text{const}$ (which works e.g. for ideal gases), then

$$U = C_V T$$

HEAT CAPACITIES

ISOBARIC HEAT CAPACITY ($p = \text{const}$):

The first law of thermodynamics ($dW = p dV \neq 0$):

$$\delta Q = dU + \delta W = C_V dT + p dV$$

Qualitatively: at $p = \text{const}$ the heat added to the system goes to *both* increasing the temperature *and* doing work. Hence $C_p > C_V$.
In a simple case where $C_V = \text{const}$ (e.g., ideal gas):

$$\begin{aligned} C_p &= \frac{\delta Q}{dT} && \text{at } p = \text{const} \\ &= C_V + p \frac{dV}{dT} && C_V = \text{const only} \\ &= C_V + p \underbrace{\left(\frac{\partial V}{\partial T} \right)_p}_{\text{to be evaluated using the EoS}} \end{aligned}$$

EXAMPLE: IDEAL GAS HEAT CAPACITIES

For ν moles of ideal gas $pV = \nu RT \Rightarrow$

$$p \left(\frac{\partial V}{\partial T} \right)_p = \nu R \Rightarrow C_p = C_V + \nu R$$

Introducing the *molar* heat capacities $C_p = \nu c_p$ and $C_V = \nu c_V$:

$$c_p = c_V + R \quad (\text{ideal gas only})$$

ADIABATIC PROCESS IN AN IDEAL GAS

The first law of thermodynamics

$$0 = \delta Q = \nu c_V dT + p dV \quad (\text{here } p \neq \text{const!})$$

Ideal gas EoS: $pV = \nu RT \Rightarrow$

$$d(pV) = p dV + V dp = \nu R dT$$

Therefore,

$$\frac{c_V}{R}(p dV + V dp) + p dV = 0$$

Define $\gamma = c_p/c_V$ and rearrange terms:

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0 \quad \Rightarrow \quad \gamma \log V + \log p = \text{const}$$

Finally, $pV^\gamma = \text{const} \quad (\text{ideal gas only})$