

Why Thermodynamics

Natural processes

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Modeling in Sciences

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geometry (shapes and behaviour of particles/system) \iff **Linear Algebra**

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Chance \iff **Probability**

Macroscopic and microscopic processes

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relevant questions :

- ▶ Why do things happen unidirectionally,
 - ▶ e.g. aging, falling of a leaf from a tree, etc.
- ▶ Is there a quantitative way of characterising spontaneity?

Microscopic Disorder \Leftarrow

dynamical laws:

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Grand journey from bi(multi)-nomial to Gaussian

Thermodynamics \Rightarrow Entropy, Free energy



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molecular dynamics : monte carlo simulations



equilibrium properties

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physical state of a sample of a substance, its physical condition
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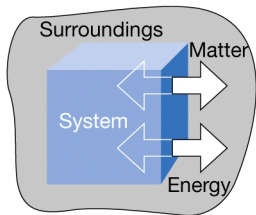
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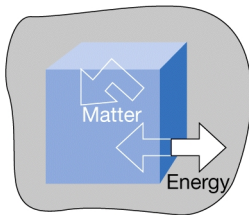
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is defined by its physical properties

Two samples of same substance with same physical properties
are in the same **state**

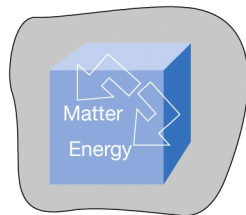
Thermodynamic systems :



(a) Open



(b) Closed



(c) Isolated

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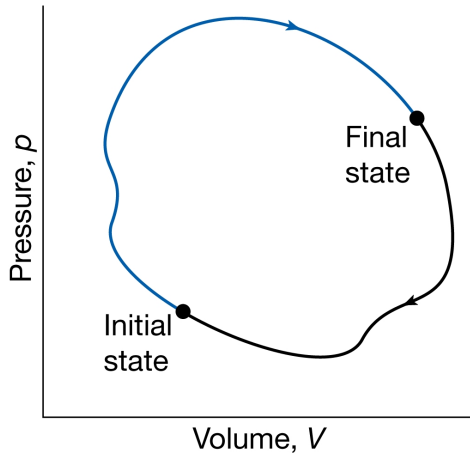
state functions

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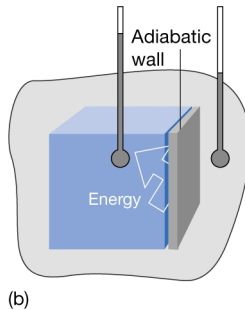
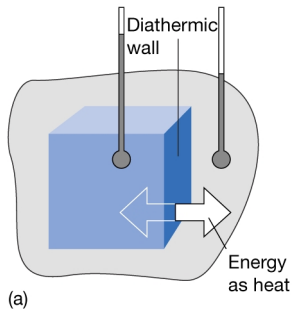
state functions

path functions

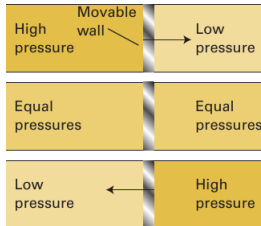
cyclic process : $\oint dX = 0$, if X is a state function



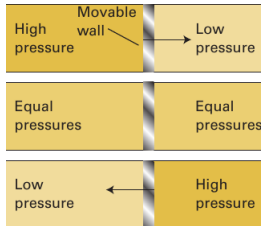
Heat flow - Diathermal and adiabatic walls :



Mechanical motion - Movable and rigid walls



Mechanical motion - **Movable** and **rigid** walls



Mass flow : **Permeable** and **impermeable** walls

What equilibrium thermodynamics **does not** deal with :

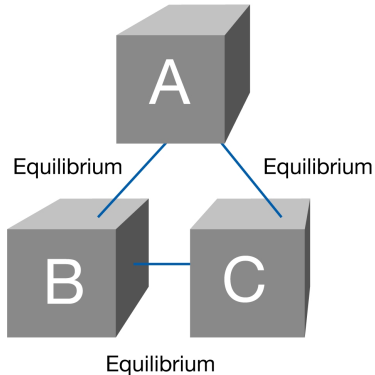
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- ▶ and rate at which processes occur

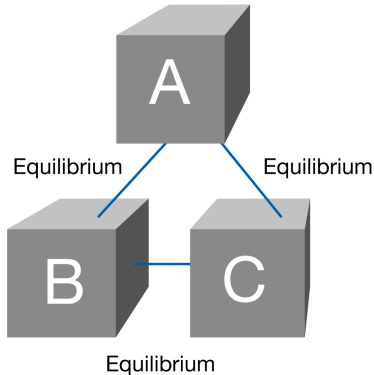
Zeroth Law of thermodynamics



If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C then systems A and C are in thermal equilibrium with each other

The qualitative observation is quantified by associating a parameter with each system, which is a real number, called Temperature

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$$\forall x_i \in \mathcal{R}, \text{ if } x_A = x_B \text{ and } x_B = x_C \implies x_A = x_C$$

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intensive property : independent of amount of substance present

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A good example of **Reductionism** in modern science

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STP : 0°C and 1 atm; molar volume of a perfect gas, $V_m = 22.414 \text{ dm}^3 \text{ mol}^{-1}$

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normal atmospheric pressure at sea level ($\approx 1 \text{ atm}$) is already low enough for most gases to behave almost perfectly

molecular explanation of Boyle's law :

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Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently

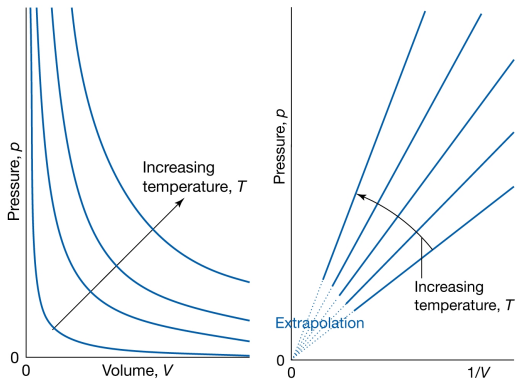
molecular explanation of Charles's law :

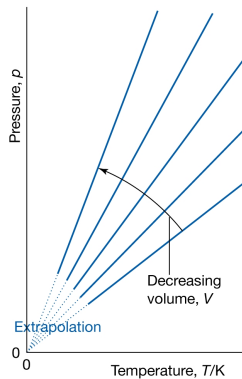
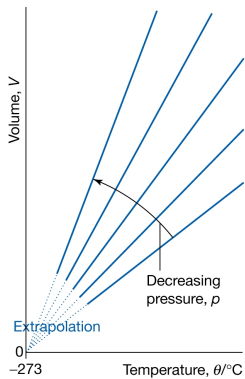
raising temperature of a gas increases average speed of molecules

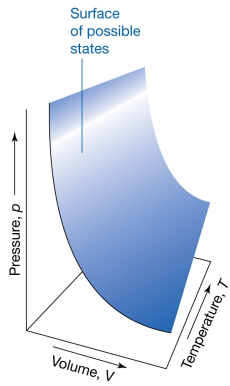
molecules collide with the walls more frequently and with greater impact

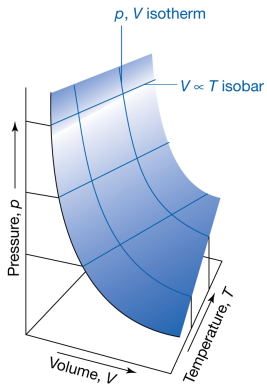
⇒ they exert a greater pressure on the walls of the container

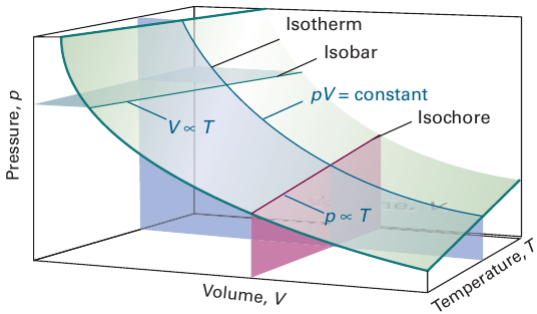
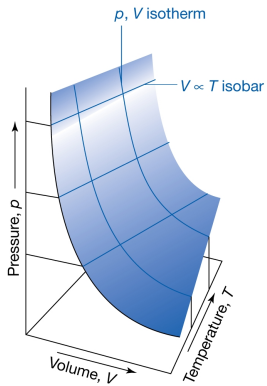
p-V-T plots : Boyle's/Charles' law and perfect gases:



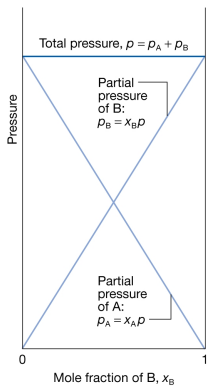




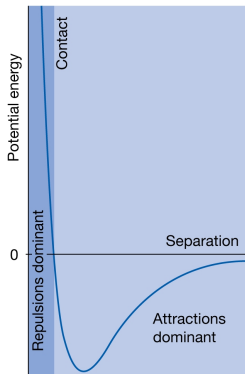




mixtures - partial pressures :



real gases :



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- ▶ volume excluded per molecule $= 4V_{\text{molecule}} \quad \therefore b = 4V_{\text{molecule}} \cdot N_A$

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solved problem : Estimate the molar volume of CO_2 at 500 K and 100 atm by treating it as a van der Waals gas , given $\left\{ \begin{array}{l} a = 3.592 \text{ dm}^6 \text{atmmol}^{-2} \\ b = 4.257 \times 10^{-2} \text{ dm}^3 \text{mol}^{-1} \end{array} \right.$

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or, $x = 0.366 \text{ dm}^3 \text{mol}^{-1}$ (perfect gas : $0.41 \text{ dm}^3 \text{mol}^{-1}$)

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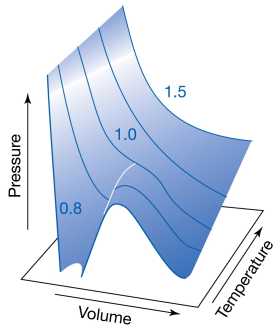
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advantage :

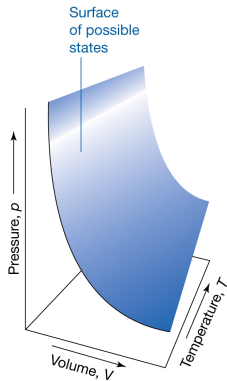
- ▶ analytical equation
- ▶ allows us to draw some general conclusions about real gases

Isotherms reflect consequences of interactions

van der Waals



perfect gas



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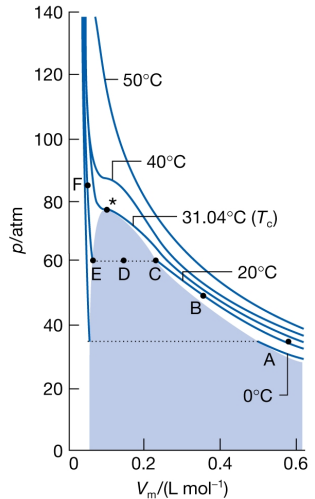
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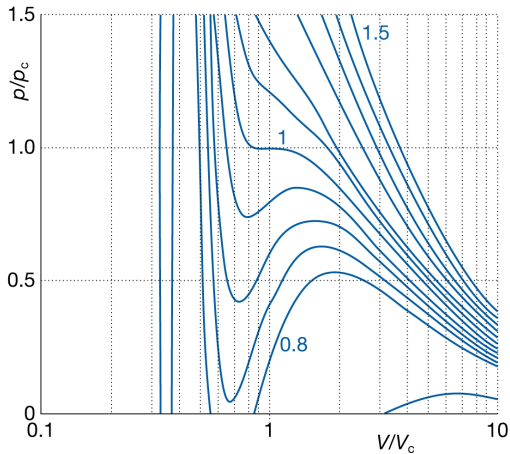
At moderate pressures, average separation of molecules is only a few molecular diameters attractive forces dominate gas is more compressible than a perfect gas because the forces help to draw the molecules together

At high pressures, average separation of molecules is small, repulsive forces dominate and the gas is less compressible because now the forces help to drive the molecules apart

experimental data for CO₂

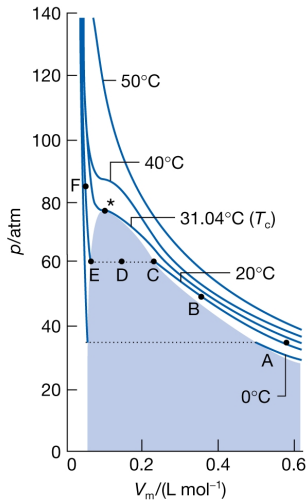


van der Waals isotherms at several values of $\frac{T}{T_c}$

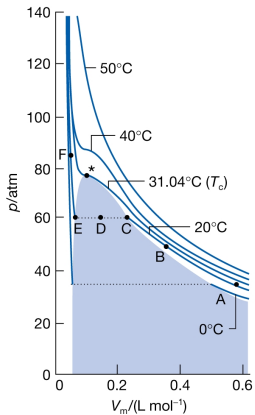


critical isotherm is for $\frac{T}{T_c} = 1$

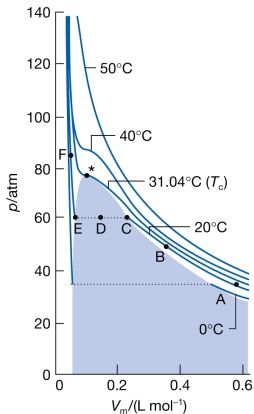
experimental data for CO_2



compress gas initially
in state A at constant
 T by pushing a piston

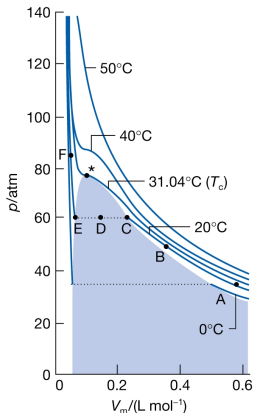


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 \approx as in Boyle's law

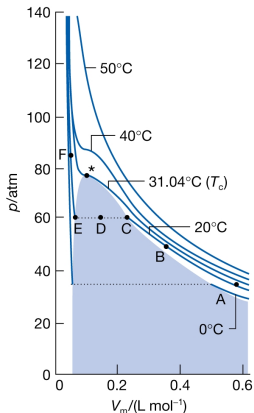
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At C ($\approx 60 \text{ atm}$ for CO_2), all similarity to perfect
behaviour is lost, for suddenly the piston slides in
without any rise in pressure: horizontal line CDE

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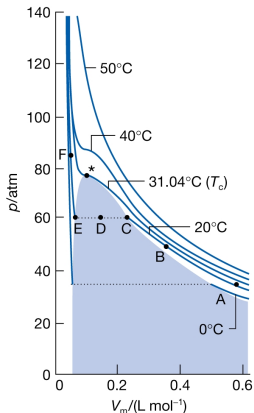


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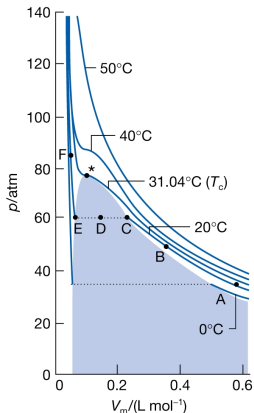
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pressure on line CDE, when both liquid and vapour
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liquid at the temperature of the experiment

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 T by pushing a piston



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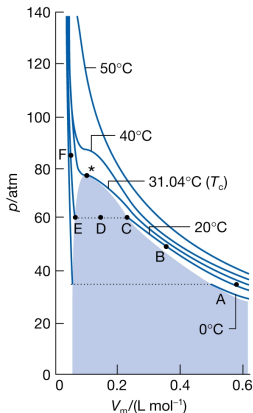
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liquid at the temperature of the experiment

At E, sample is entirely liquid and the piston rests on
its surface

compress gas initially
in state A at constant
 T by pushing a piston



Near A, pressure rises
 \approx as in Boyle's law

At C ($\approx 60 \text{ atm}$ for CO_2), all similarity to perfect
behaviour is lost, for suddenly the piston slides in
without any rise in pressure: horizontal line CDE

just to the left of C, liquid appears, and there are two
phases separated by a sharply defined surface. As
volume is decreased from C through D to E, the
amount of liquid increases

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considerable pressure

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The single phase that fills the entire volume when $T > T_C$ may be much denser than typical gas : supercritical fluid

features of the van der Waals eqn

(1) Perfect gas isotherms obtained at high T and large V_m

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \xrightarrow[\text{high } T]{V_m \gg b} \quad \frac{RT}{V_m}$$

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(3) critical constants related to van der Waals coefficients

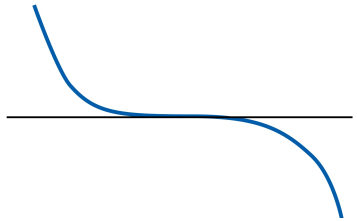
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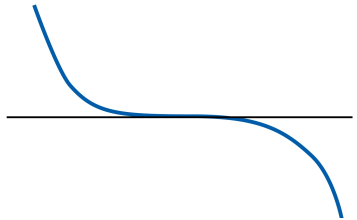
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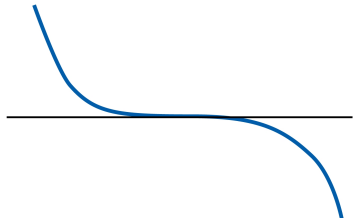
using $\frac{dp}{dV_m} = \frac{d^2p}{dV_m^2} = 0$

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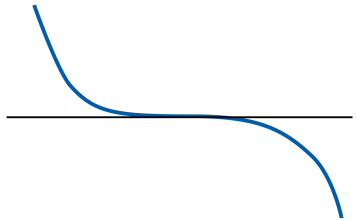
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Below a critical temperature, T_C , van der Waals isotherms show oscillations

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$$p = p_r p_C; V = V_r V_C; T = T_r T_C$$

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works best for gases composed of spherical molecules
fails when the molecules are non-spherical or polar

The principle of corresponding states :

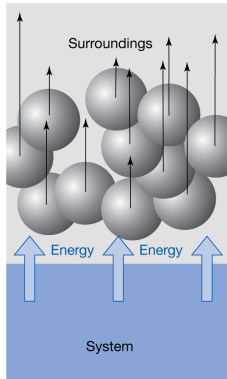
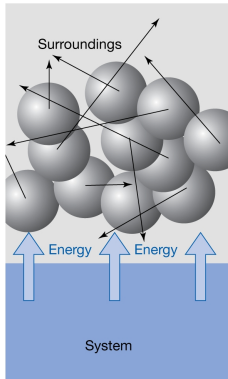
	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p = \frac{nRT}{V}$				
van der Waals	$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$	$p_r = \frac{8T_r}{3V_r-1} - \frac{3}{V_r^2}$	$\frac{a}{27b^2}$	$3b$	$\frac{8a}{27bR}$
Berthelot	$p = \frac{nRT}{V-nb} - \frac{n^2a}{TV^2}$	$p_r = \frac{8T_r}{3V_r-1} - \frac{3}{T_r V_r^2}$	$\frac{1}{12} \left(\frac{2aR}{3b^3} \right)^{1/2}$	$3b$	$\frac{2}{3} \left(\frac{2a}{3bR} \right)^{1/2}$
Dieterici	$p = \frac{nRT e^{-aRTV/n}}{V-nb}$	$p_r = \frac{T_r e^{2(1-1/T_r V_r)}}{2V_r-1}$	$\frac{a}{4e^2 b^2}$	$2b$	$\frac{a}{4bR}$
Virial	$p = \frac{nRT}{V} \left\{ 1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2} + \dots \right\}$				

critical constants : typical values

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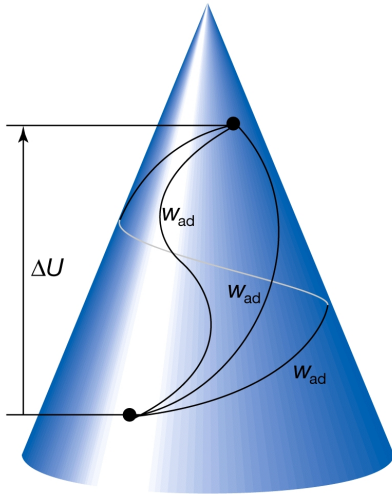
gas	p_c atm	V_c cm^3	T_c K	$Z_c = \frac{pV_m}{RT}$	T_B K
Ar	48.0	75.3	150.7	0.292	411.5
CO ₂	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O ₂	50.14	78.0	154.8	0.308	405.9

Heat and work :

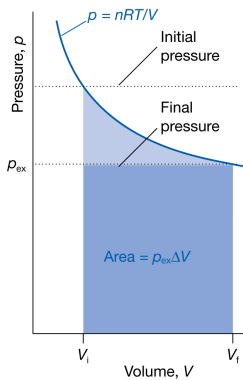
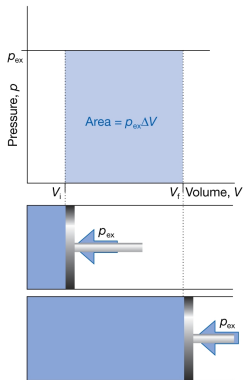


path functions: work

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Calculating work :



Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

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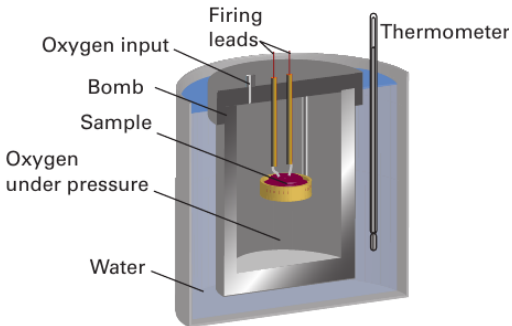
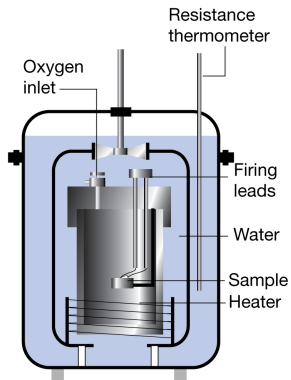
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$$dU = dq_V$$

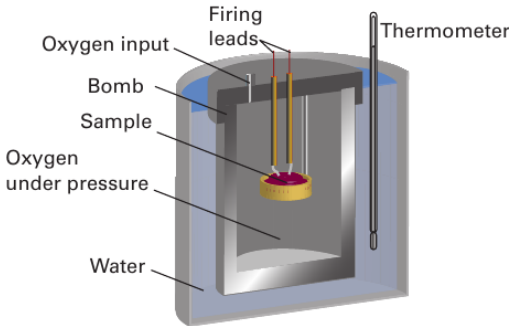
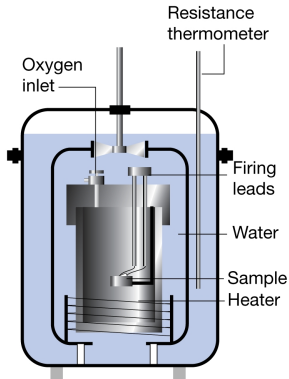
Calorimetry

- Constant volume bomb calorimeter : measurement of q_V



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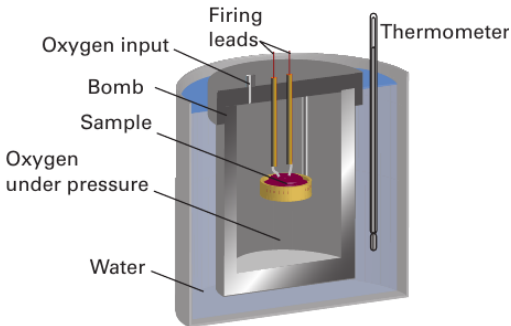
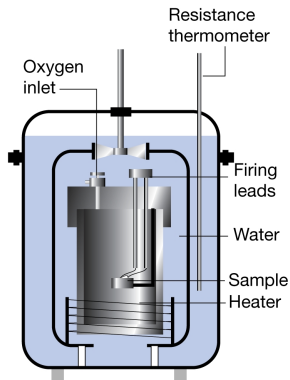
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To ensure adiabaticity, calorimeter is immersed in a water bath with temperature continuously readjusted to that of calorimeter at each stage of combustion

change in calorimeter temperature, $\Delta T \propto$ energy released or absorbed in reaction

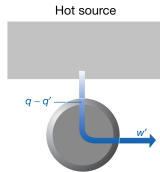
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Calibration : use a process of known energy output and determine calorimeter constant

$$q = C\Delta T$$

Thermodynamic engine :



Type of work	dw	Comments	Units [†]
Expansion	$-p_{\text{ex}}dV$	p_{ex} is the external pressure dV is the change in volume	Pa m ³
Surface expansion	$\gamma d\sigma$	γ is the surface tension $d\sigma$ is the change in area	N m ⁻¹ m ²
Extension	$f dl$	f is the tension dl is the change in length	N m
Electrical	ϕdQ	ϕ is the electric potential dQ is the change in charge	V C
	$Q d\phi$	$d\phi$ is the potential difference Q is the charge transferred	V C

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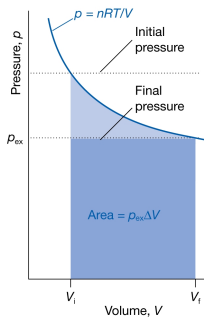
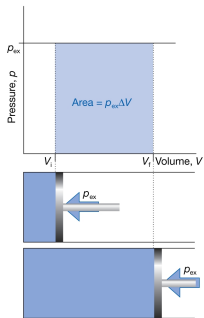
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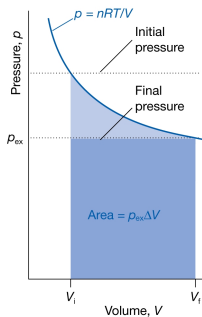
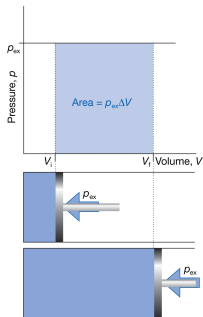
Such a system is **not** in mechanical equilibrium

Calculating work :



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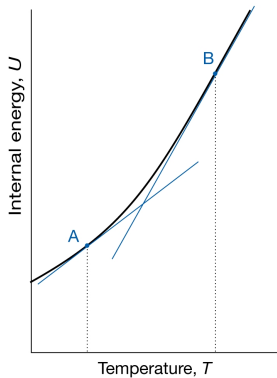
For a perfect gas, reversible work of expansion =

$$\begin{aligned}
 - \int_{V_i}^{V_f} p_{\text{ext}} dV &= - \int_{V_i}^{V_f} p dV \\
 &= -nRT \ln \frac{V_f}{V_i}
 \end{aligned}$$

for spontaneous expansion :

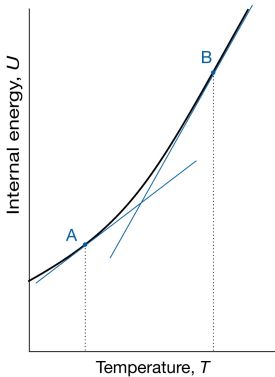
$$\text{work} = -p_{\text{ext}} (V_f - V_i)$$

Internal energy (U) as a function of temperature : $U(V, T)$



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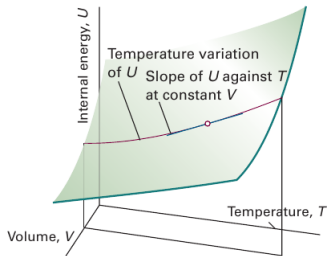


internal energy of a system
increases as temperature is raised
slope of tangent at any
temperature = heat capacity, C

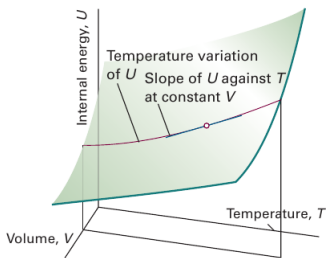
in the Fig.,

$$C \text{ at A} < C \text{ at B}$$

$$U(V, T)$$

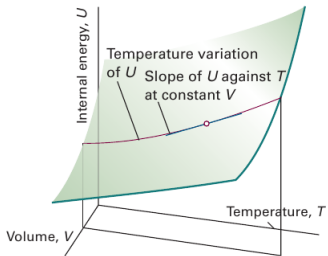


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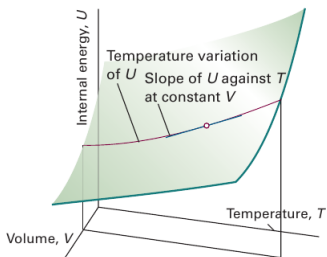
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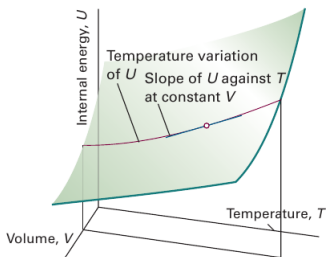


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If heat capacity is independent of temperature over range of temperatures of interest
then $\Delta U = C_V \Delta T$