

## 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  $\Leftarrow$

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molecular dynamics : monte carlo simulations



equilibrium properties

## Thermodynamic space

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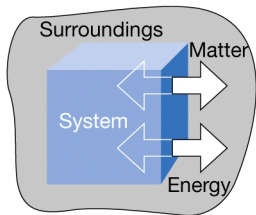
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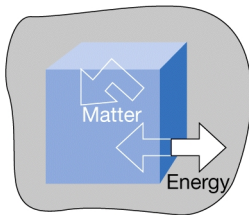
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Two samples of same substance with same physical properties  
are in the same **state**

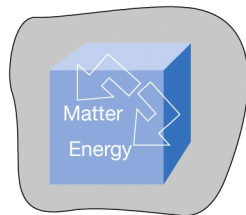
## Thermodynamic systems :



(a) Open



(b) Closed



(c) Isolated

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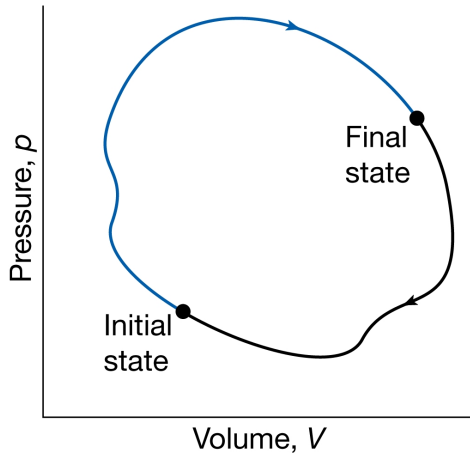
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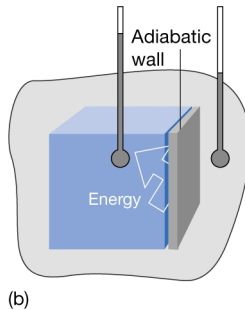
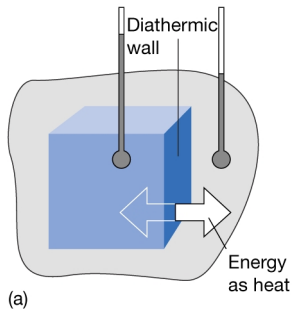
**path** functions



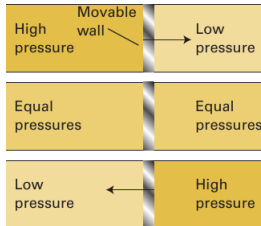
cyclic process :  $\oint dX = 0$  , if  $X$  is a state function



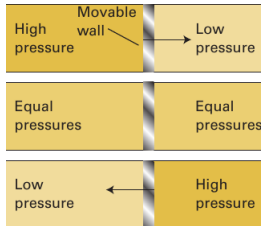
## Heat flow - Diathermal and adiabatic walls :



## 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 :

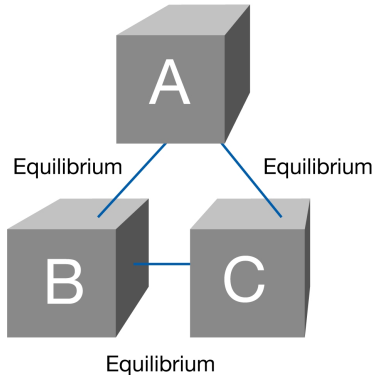
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- ▶ time
- ▶ and rate at which processes occur

## Zeroth Law of thermodynamics

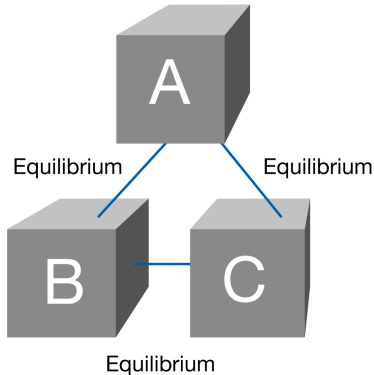


If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C then systems A and C are in thermal equilibrium with each other

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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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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

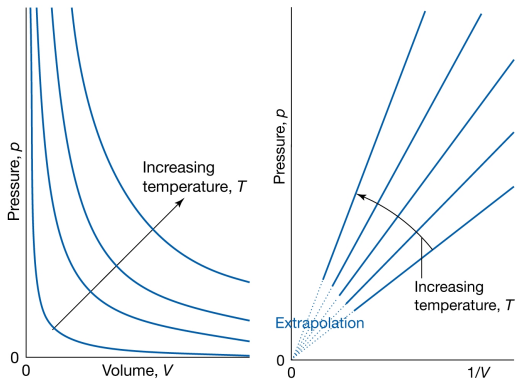
molecular explanation of Charles's law :

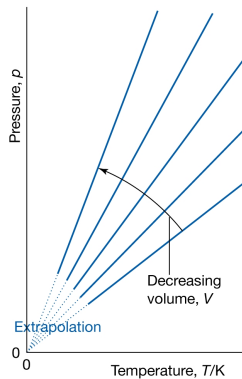
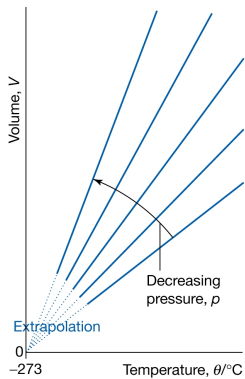
raising temperature of a gas increases average speed of molecules

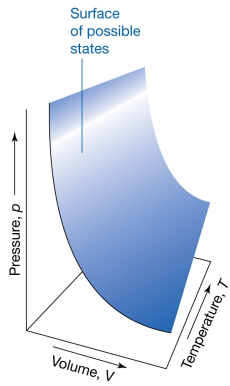
molecules collide with the walls more frequently and with greater impact

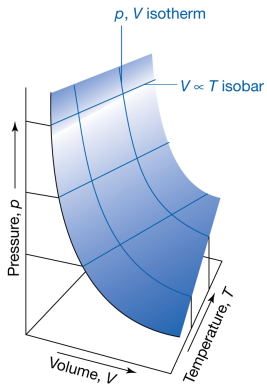
⇒ they exert a greater pressure on the walls of the container

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

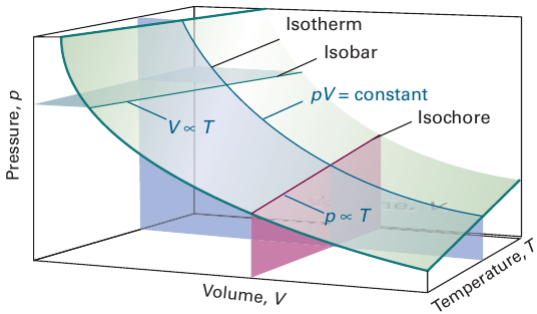
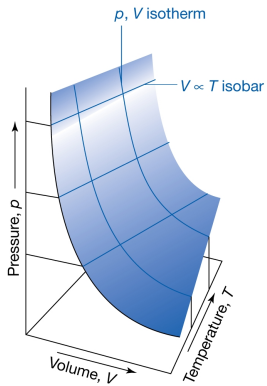




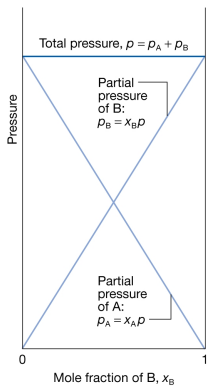




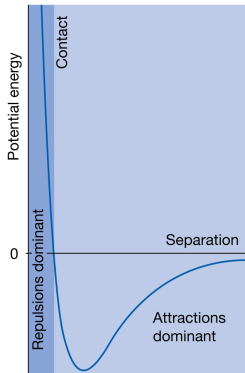




mixtures - partial pressures :



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  $\text{CO}_2$  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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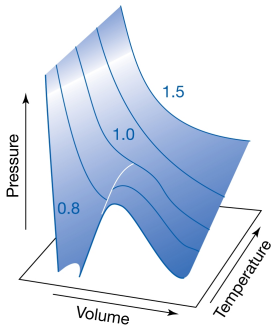
advantage :

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

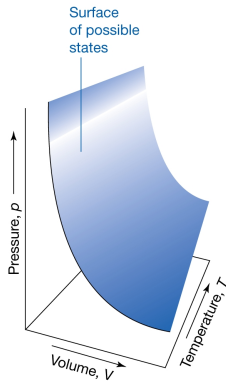


Isotherms reflect consequences of interactions

van der Waals



perfect gas



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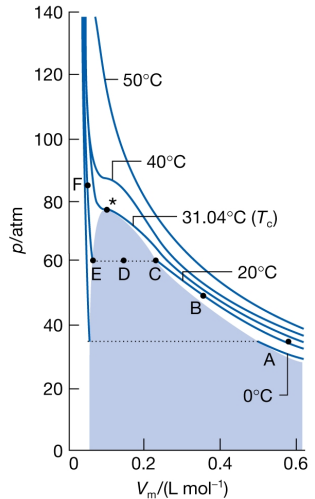
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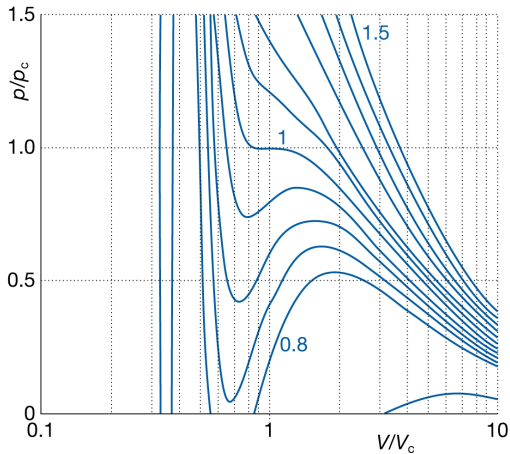
At moderate pressures, average separation of molecules is only a few molecular diameters attractive forces dominate gas is more compressible than a perfect gas because the forces help to draw the molecules together

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 CO<sub>2</sub>

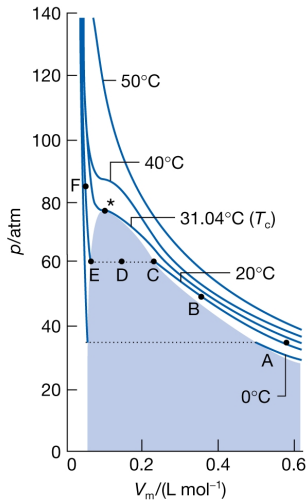


van der Waals isotherms at several values of  $\frac{T}{T_c}$

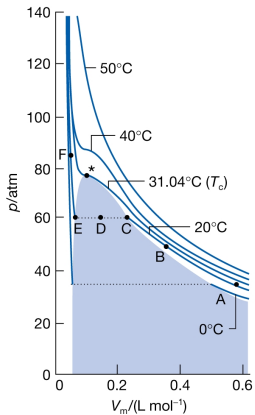


critical isotherm is for  $\frac{T}{T_c} = 1$

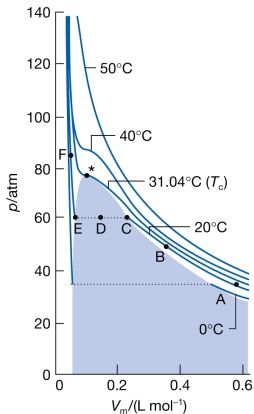
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compress gas initially  
in state A at constant  
 $T$  by pushing a piston



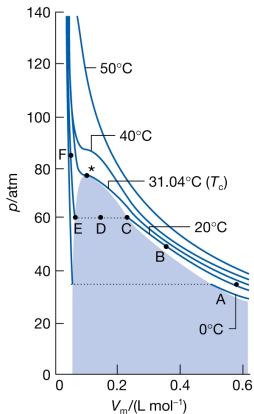
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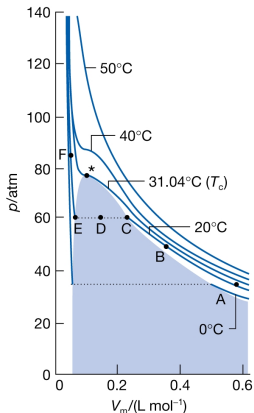
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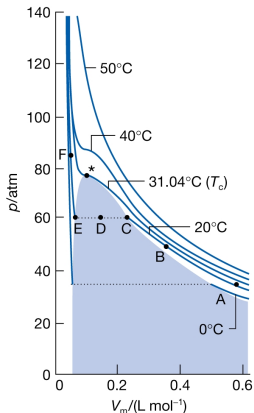


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just to the left of C, liquid appears, and there are two  
phases separated by a sharply defined surface. As  
volume is decreased from C through D to E, the  
amount of liquid increases

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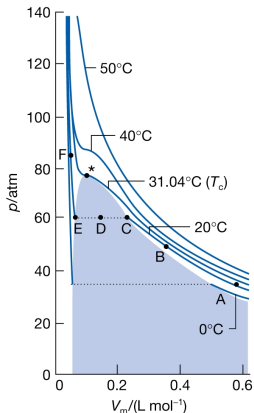
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At C ( $\approx 60$  atm for  $\text{CO}_2$ ), all similarity to perfect  
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without any rise in pressure: horizontal line CDE

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  
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pressure on line CDE, when both liquid and vapour  
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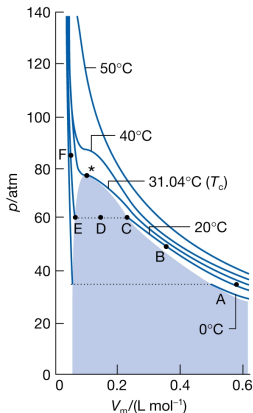
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The single phase that fills the entire volume when  $T > T_C$  may be much denser than typical gas : supercritical fluid

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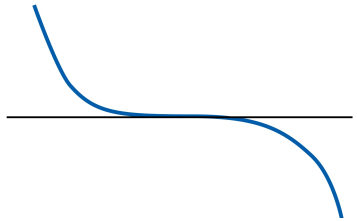
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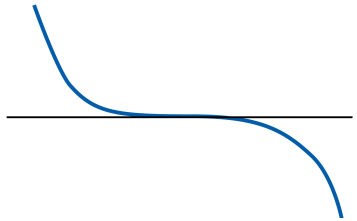
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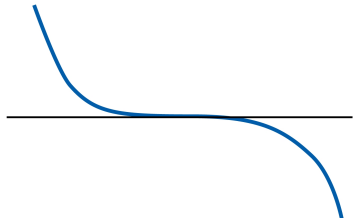
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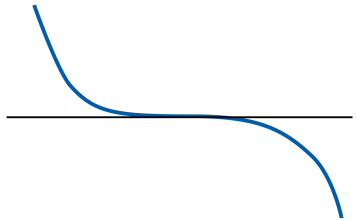
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Below a critical temperature,  $T_C$ , van der Waals isotherms show oscillations

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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 : (Note: the expression for Dieterici equation below is incorrect. The correct expression is :  $p = \frac{nRTe^{-\frac{na}{RTV}}}{V-nb}$ )

	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	$p = \frac{nRTe^{-aRTV/n}}{V-nb}$	$p_r = \frac{T_r e^{2(1-1/T_r V_r)}}{2V_r-1}$	$\frac{a}{4e^2 b^2}$	$2b$	$\frac{a}{4bR}$
Virial	$p = \frac{nRT}{V} \left\{ 1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2} + \dots \right\}$				

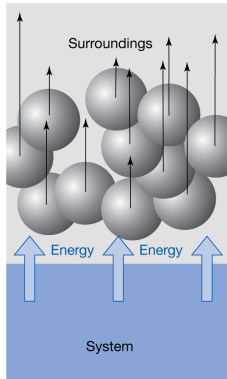
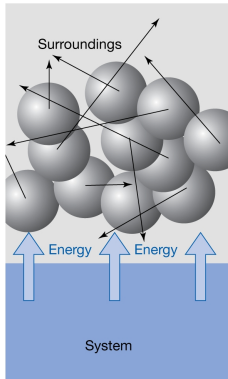
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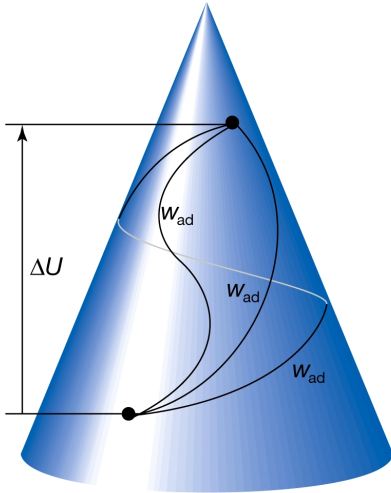
gas	$p_c$ atm	$V_c$ $\text{cm}^3$	$T_c$ K	$Z_c = \frac{pV_m}{RT}$	$T_B$ K
Ar	48.0	75.3	150.7	0.292	411.5
CO <sub>2</sub>	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O <sub>2</sub>	50.14	78.0	154.8	0.308	405.9

## Heat and work :

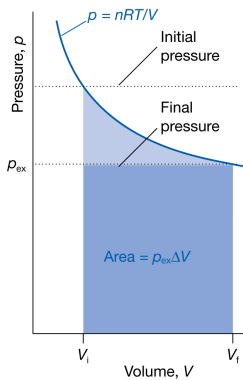
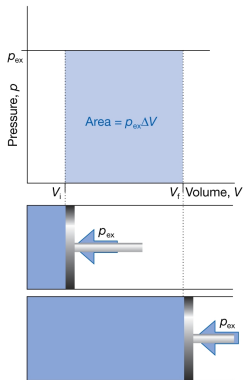


path functions: work

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## Calculating work :



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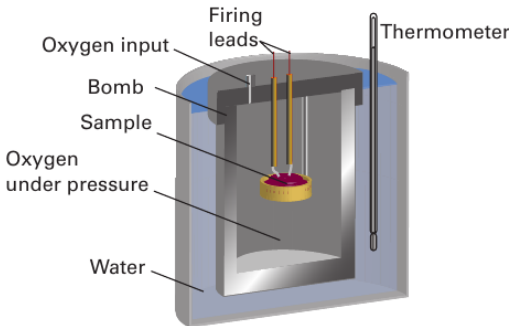
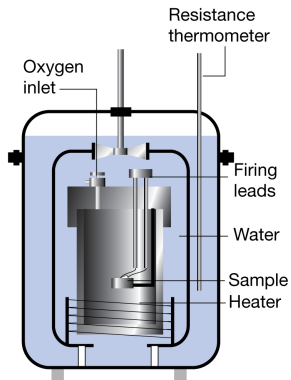
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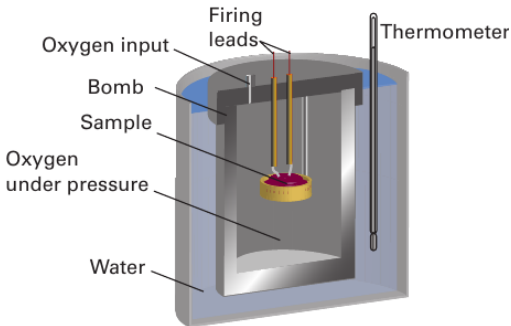
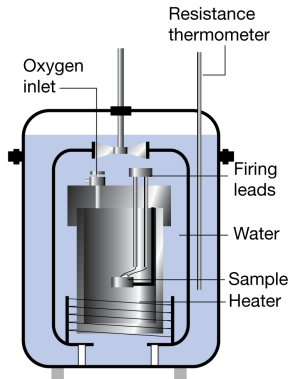
## Calorimetry

- Constant volume bomb calorimeter : measurement of  $q_V$



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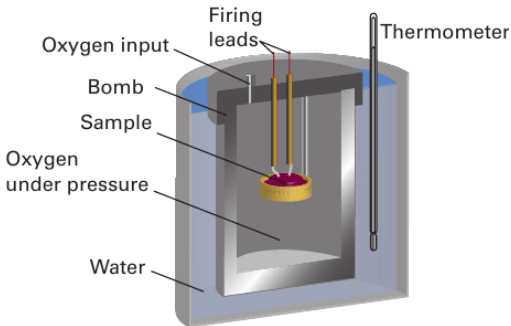
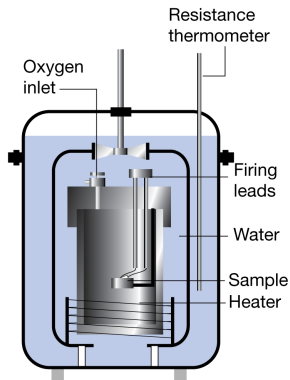
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To ensure adiabaticity, calorimeter is immersed in a water bath with temperature continuously readjusted to that of calorimeter at each stage of combustion

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



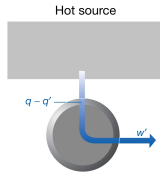
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Calibration : use a process of known energy output and determine calorimeter constant

$$q = C\Delta T$$

Thermodynamic engine :



Type of work	$dw$	Comments	Units <sup>†</sup>
Expansion	$-p_{\text{ex}}dV$	$p_{\text{ex}}$ is the external pressure $dV$ is the change in volume	Pa m <sup>3</sup>
Surface expansion	$\gamma d\sigma$	$\gamma$ is the surface tension $d\sigma$ is the change in area	N m <sup>-1</sup> m <sup>2</sup>
Extension	$f dl$	$f$ is the tension $dl$ is the change in length	N m
Electrical	$\phi dQ$	$\phi$ 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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If, on the other hand, the external pressure differs measurably from the internal pressure, then changing  $p_{\text{ex}}$  infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process.

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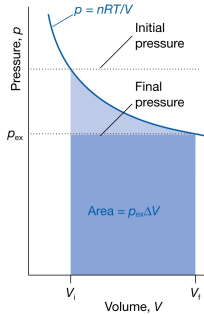
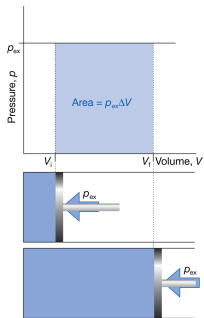
If the external pressure is increased infinitesimally, the gas contracts slightly

In either case the change is reversible in the thermodynamic sense

If, on the other hand, the external pressure differs measurably from the internal pressure, then changing  $p_{\text{ex}}$  infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process.

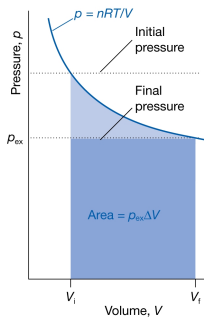
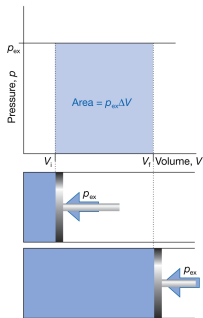
Such a system is **not** in mechanical equilibrium

Calculating work :



For a perfect gas, reversible work of expansion =

## Calculating work :



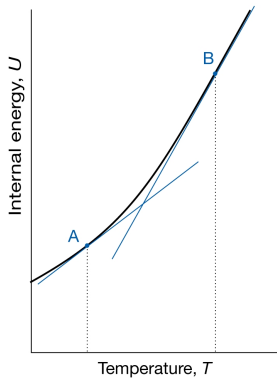
For a perfect gas, reversible work of expansion =

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

for spontaneous expansion :

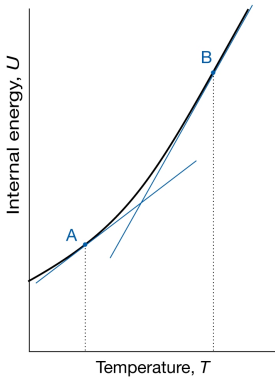
$$\text{work} = -p_{\text{ext}} (V_f - V_i)$$

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



internal energy of a system  
increases as temperature is raised

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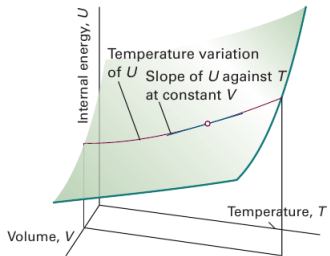
internal energy of a system  
increases as temperature is raised  
slope of tangent at any  
temperature = heat capacity,  $C$

in the Fig.,

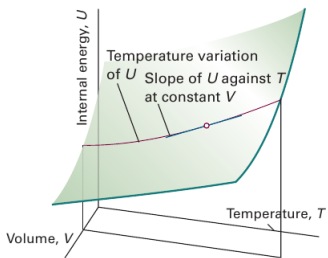
$$C \text{ at A} < C \text{ at B}$$



$$U(V, T)$$

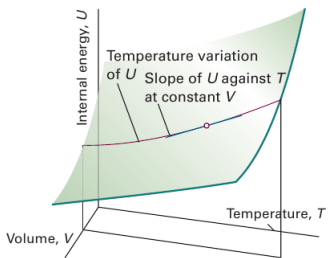


$$U(V, T)$$



$$C_V = \left( \frac{dq}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$

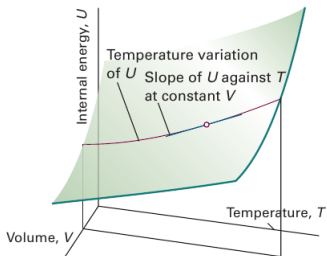
$$U(V, T)$$



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$$\Rightarrow dU = C_V dT$$

$$U(V, T)$$

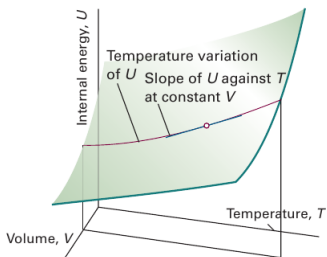


$$C_V = \left( \frac{dq}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$

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If heat capacity is independent of temperature over range of temperatures of interest

$$U(V, T)$$



$$C_V = \left( \frac{dq}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$

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