

Chapter 2. The First Law of Thermodynamics

2.A.1. Heat, Work, and Energy

Newton's first law: The velocity is conserved in magnitude and direction in the absence of an external force: $E_k = \frac{1}{2}mv^2$ is conserved.

Newton's second law:

$$F = m \frac{dv}{dt} = ma$$

If a body moves a distance dx through a force field $F(x)$, the change of the kinetic energy is

$$\int_{x_1}^{x_2} F(x)dx = m \int_{x_1}^{x_2} \frac{dv}{dx} dx = m \int_v^v v dv = \frac{1}{2} m(v_2^2 - v_1^2)$$

so

$$\int_{x_1}^{x_2} F(x)dx = \frac{1}{2} mv_2^2 - \frac{1}{2} mv_1^2 = E_{k_2} - E_{k_1}$$

This change is the work done on the body by outside forces:

$$w = \int_{x_1}^{x_2} F(x) dx$$

If this force is a function of x alone, not of time, the force can be related to a potential energy function $U(x)$:

$$F = - \frac{dU(x)}{dx}$$

$$E_{k_2} + U(x_2) = E_{k_1} + U(x_1)$$

The total energy, the sum of the kinetic energy plus the potential energy, is conserved.

2.A.4(b). Heat Capacity

Heat: Extensive Property

Temperature: Intensive Property

$$C \equiv \frac{dQ}{dT}$$

*Eq. (2A.14)
Explanation
not right*

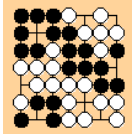
For electrical heat,

$q = I^2 R t$: Joule's law of electrical heating

$C = \frac{q}{\Delta T}$: **Heat Capacity** [Meaning vs. Definition]

$C(T)$

$C(T) = \frac{dq}{dT}$: The heat capacity is a function of temperature.



$$C_V \equiv \left(\frac{dq}{dT} \right)_V$$

heat capacity at constant volume - *Theoretician*

$$C_p \equiv \left(\frac{dq}{dT} \right)_p$$

heat capacity at constant pressure - *Experimentalist*

$$C_{V,m} = \frac{1}{n} \left(\frac{dq}{dT} \right)_V$$

heat capacity per mole at constant volume

$$C_{p,m} = \frac{1}{n} \left(\frac{dq}{dT} \right)_p$$

molar heat capacity at constant pressure



"I take my blood pressure medicine at bedtime and before looking at the market reports."

2.A.2. Internal Energy Function, U

System: Some part of the world that we are interested, and plan to describe thermodynamically.

Surroundings: The rest of the world outside the system.

Closed System: In which the transfer of matter to and from the surroundings is forbidden. Energy may be exchanged between a closed system and the surroundings.

δN_j

Isolated System: When a closed system cannot work nor exchange heat with its surroundings.

δU

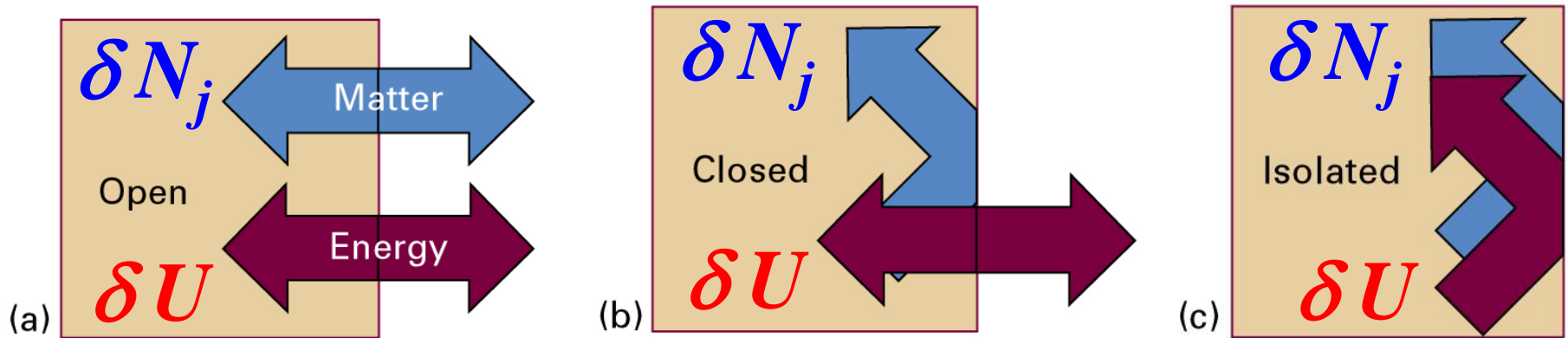


Figure 2.A.1

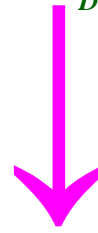
- (a) An open system can exchange matter and energy with its surroundings.
- (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter.
- (c) An isolated system can exchange neither energy nor matter with its surroundings.

Depending on the textbook

U : internal energy function

w : an amount of work

q : heat



There is no free lunch!

The First Law: $dU = dq + dw$ (2.A.2)

Reversible or Irreversible

The sign convention

(+): flow into the system

(-): flow out from the system

James P. Joule:

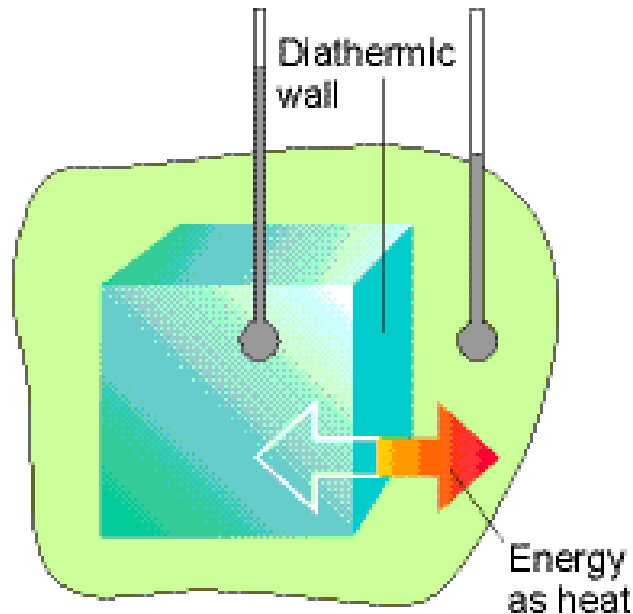
- Combined mechanical and caloric components.
- Heat is simply one form of energy.
- The total energy of an isolated system is conserved.

Energy

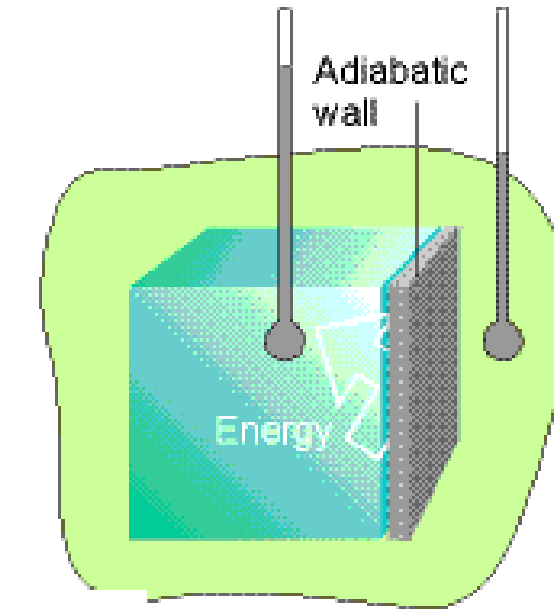
- Binding energy (by the mass difference: Einstein's Δmc^2)

adiabatic

$$dq = 0$$



(a)



(b)

- (a) A **diathermic system** is one that allows energy to escape as heat through its boundary if there is a difference in temperature between the system and its surroundings (**'dia' = through**).
- (b) An **adiabatic system** is one that does not permit the passage of energy as heat through its boundary even if there is a temperature difference between the system and its surroundings.

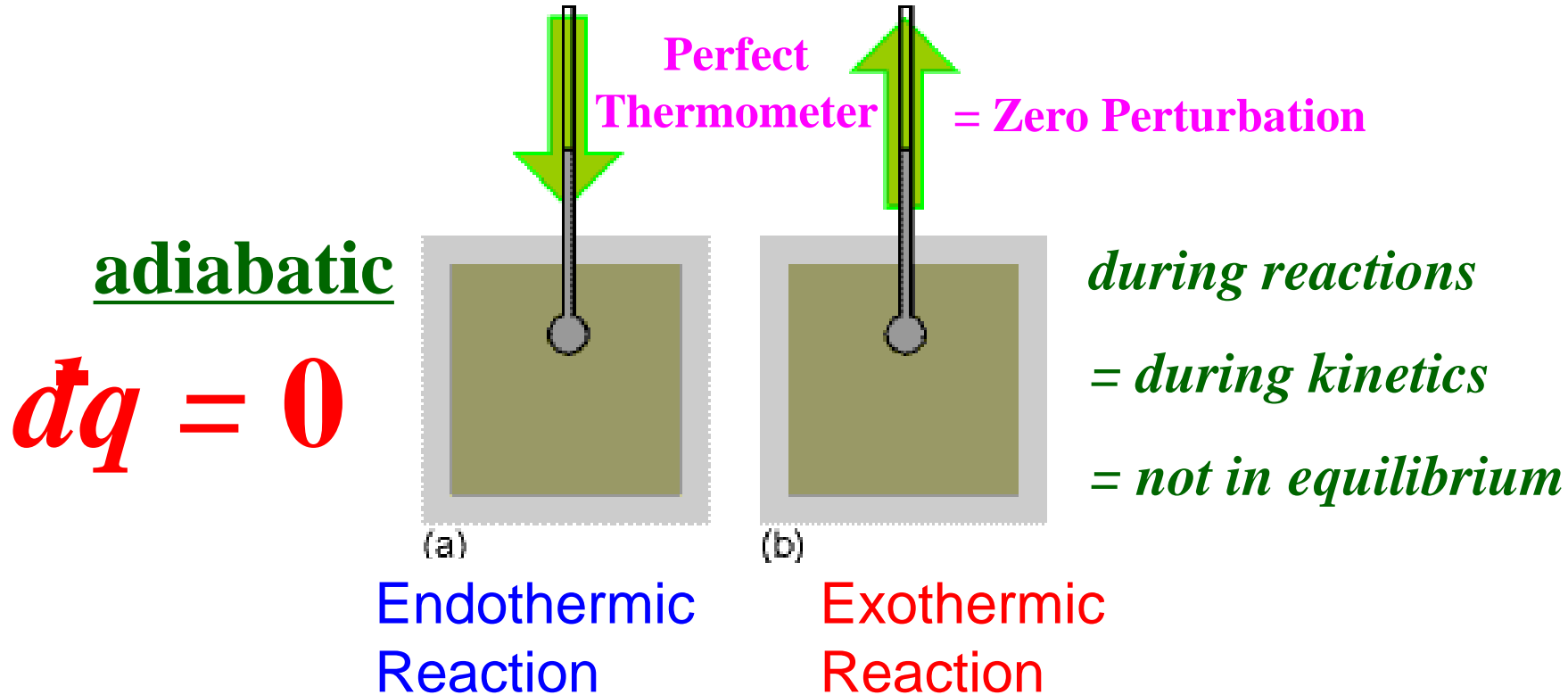


Figure 2.A.2

- (a) When an endothermic reaction occurs in an adiabatic system, the temperature falls.
- (b) If the reaction is exothermic, then the temperature rises.

2.A.3. Work

If the position moves from a position x_1 to x_2

against an opposing force F , the work will be:

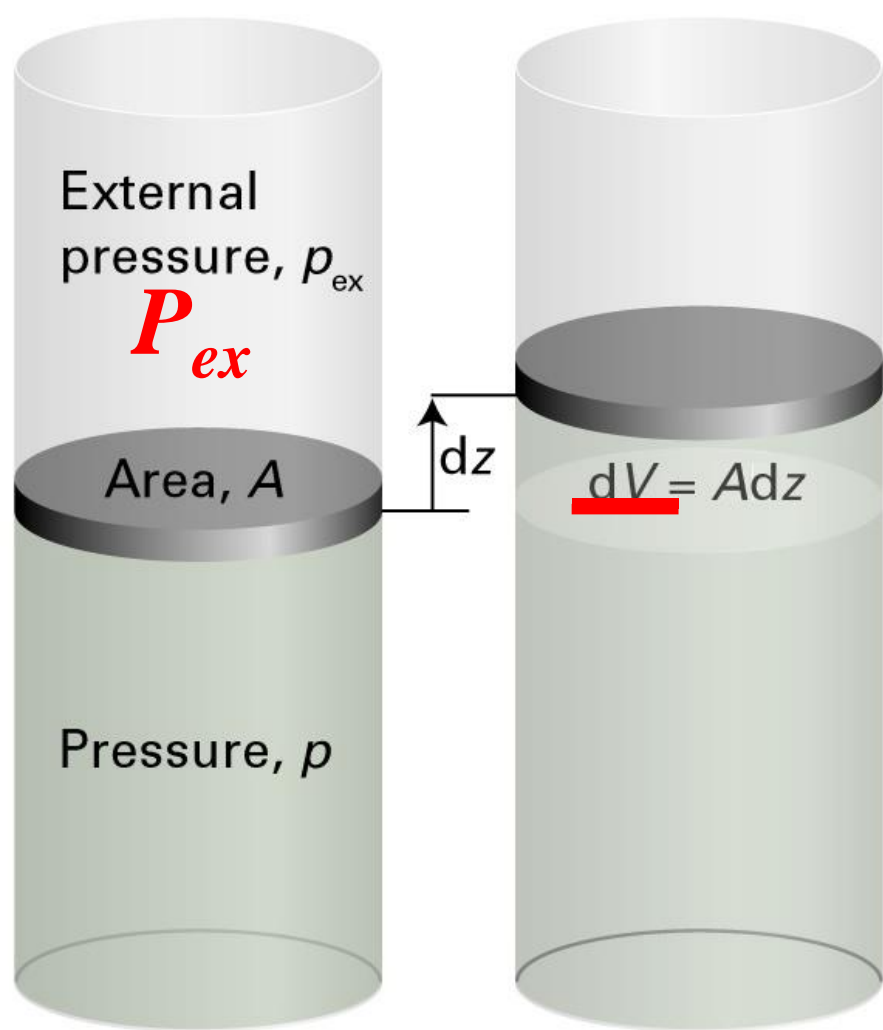
$$w = -\int_{x_1}^{x_2} F dx$$

The negative sign in this equation confirms to our stated convention that work done by the gas is **negative**.

The opposing pressure: $p_{ex} = \frac{F}{A}$ *Expansion work*

$$w = -\int_{x_1}^{x_2} F dx = -\int_{x_1}^{x_2} p_{ex} A dx = -\int_{V_1}^{V_2} p_{ex} dV, \text{ where } dV = A dx$$

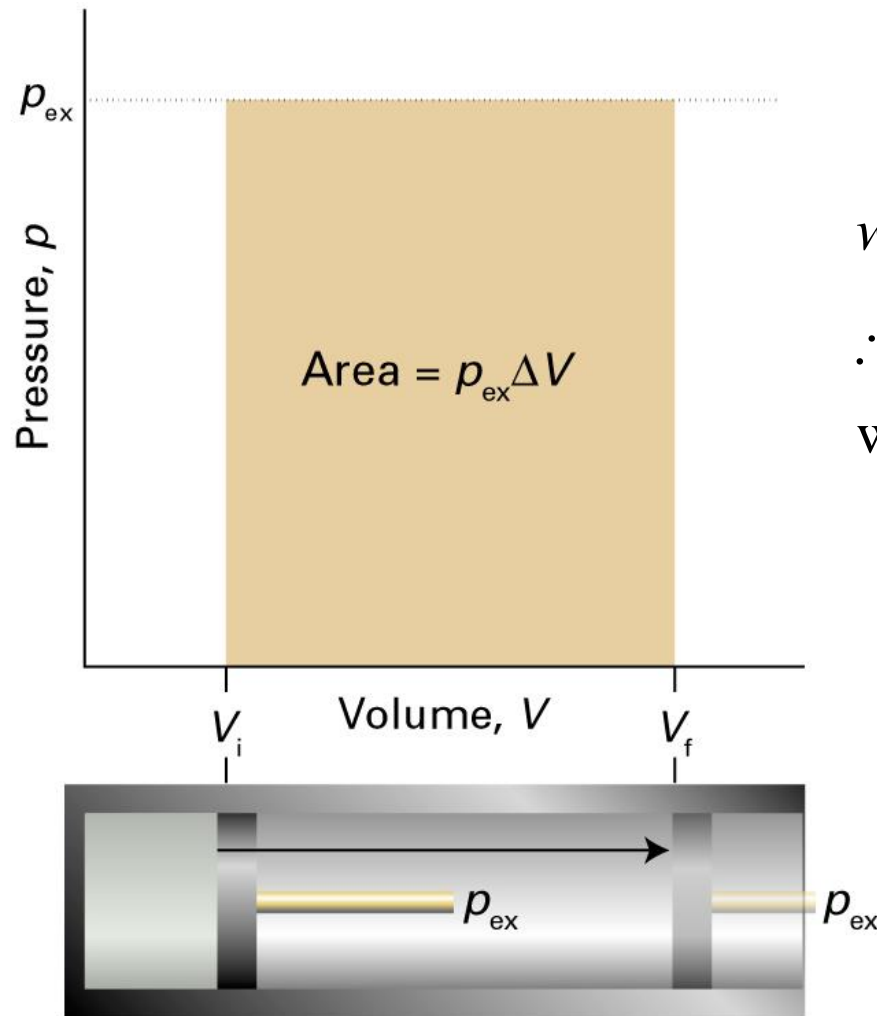
$$\underline{dw = -p_{ex} dV}$$



$$work = -p_{ex}\Delta V$$

Figure 2.A.5

When a piston of area A moves out through a distance dz , it sweeps out a volume $dV = A dz$. The external pressure, p_{ex} , is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.



$$w = -\int_{V_i}^{V_f} p_{ex} dV = -p_{ex} \int_{V_i}^{V_f} dV = -p_{ex} (V_f - V_i)$$

\therefore The work done on the system is

$$w = -p_{ex} \Delta V$$

Figure 2.A.6

The work done by a gas when it expands

against a constant external

pressure, p_{ex} , is equal to the shaded area in this example of an indicator diagram.

Table 2.A.1

Table 2.1 Varieties of work*

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	$\gamma d\sigma$	<u>γ is the surface tension</u> $d\sigma$ 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

* In general, the work done on a system can be expressed in the form $dw = -Fdz$, where F is a ‘generalized force’ and dz is a ‘generalized displacement’.

† For work in joules (J). Note that $1 \text{ N m} = 1 \text{ J}$ and $1 \text{ V C} = 1 \text{ J}$.

Surface Tension = Interfacial Free Energy

$$N/m = J/m^2 \approx eV/(2 \text{ \AA})^2$$



2.A.3(c). Reversible Expansion

Equilibrium

In thermodynamics, a reversible change is one that can be reversed by an infinitesimal modification of a variable.

$$\underline{p_{ex} \approx p_{in}}$$

$$dw = -p_{ex} dV = -p_{in} dV \quad (2A.8a)$$

$$w = -\int_{V_i}^{V_f} p_{in} dV$$

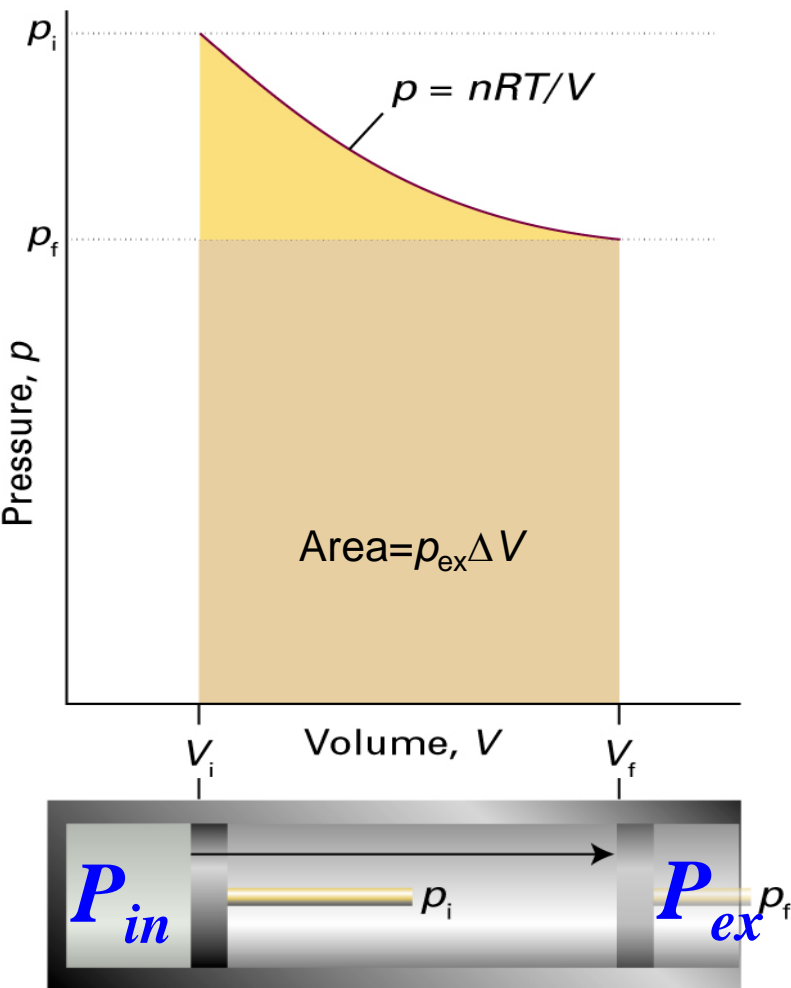
where p_{in} may be a function of volume.

One example of reversibility:

$$T_{ex} \cong T_{in}$$

Thermal equilibrium of two systems with the same temperature.

Isothermal Reversible Expansion



For ~~isothermally reversible~~ process,

$$p_{ex} \approx p_{in}$$

$$dw = -p_{ex} dV = -p_{in} dV$$

$$w = -\int_{V_i}^{V_f} p_{in} dV$$

$$pV = nRT \text{ (ideal gas)}$$

(Ideal Gas)

$$w = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

Figure 2A.7

The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$.

Area = $p_{ex} \Delta V$

The work done during the irreversible expansion against the same final pressure is equal to the rectangular area (shown darker).

Note that the reversible work is greater than the irreversible work.

$$P_{ex} \neq P_{in}$$

$$T_{ex} = T_{in}$$

Isothermal Reversible or Irreversible Expansion

$$P_{ex} \neq P_{in}$$

$$T_{ex} = T_{in}$$

Expansion work

$$w = -\int_{V_1}^{V_2} p_{ex} dV$$

The larger the opposing pressure (for a given ΔV), the more work will be done.

There is a limit to how large P_{ex} can be, of course, since if it is greater than the pressure of the driving gas (P_{in}), no expansion will occur at all.

How can the work be maximized?

Consider an ideal gas in a cylinder with a movable piston, with the pressure $p_i = 10 \text{ atm}$ and volume $V_i = 1 \text{ m}^3$. Let us assume that the opposing pressure (also 10 atm at the start) consists of 1 atm due to the air outside and 9 atm due to nine weights sitting on the piston (each exerting 1 atm pressure). **If all the weights are removed at once (suddenly)**, the gas will expand against the constant $p_i = 1 \text{ atm}$ until its pressure is 1 atm – that is, until it reaches equilibrium. If the expansion is isothermal, its final volume will be 10 m^3 , and the work done is:

$$dw = -(1 \text{ atm})(10 - 1) \text{ m}^3 = -9 \text{ m}^3 \text{ atm}$$

As a function of
two independent parameters

$U(T, V)$: internal energy

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Reversible State Function
Exact Differential

From the first law [Reversible or Irreversible]

$$dU = \bar{d}q + \bar{d}w = \bar{d}q - \underbrace{p_{\text{ex}} dV}_{pV \text{ work}} + \underbrace{\bar{d}w_e}_{\text{any other work (e.g. electrochemical)}}$$

At constant volume, no other work:

$$dU = \bar{d}q$$

$$\underline{C(T, t) \equiv \frac{\bar{d}q}{dT}}$$

$$\underline{\therefore C_V = \left(\frac{\partial U}{\partial T} \right)_V}$$

Derivation of Eq. (2A.14)
Never Definition

Time dependent
or
Time independent

$U = U(T, V)$ vs. $U = U(T, V, time)$

Equilibrium

Nonequilibrium

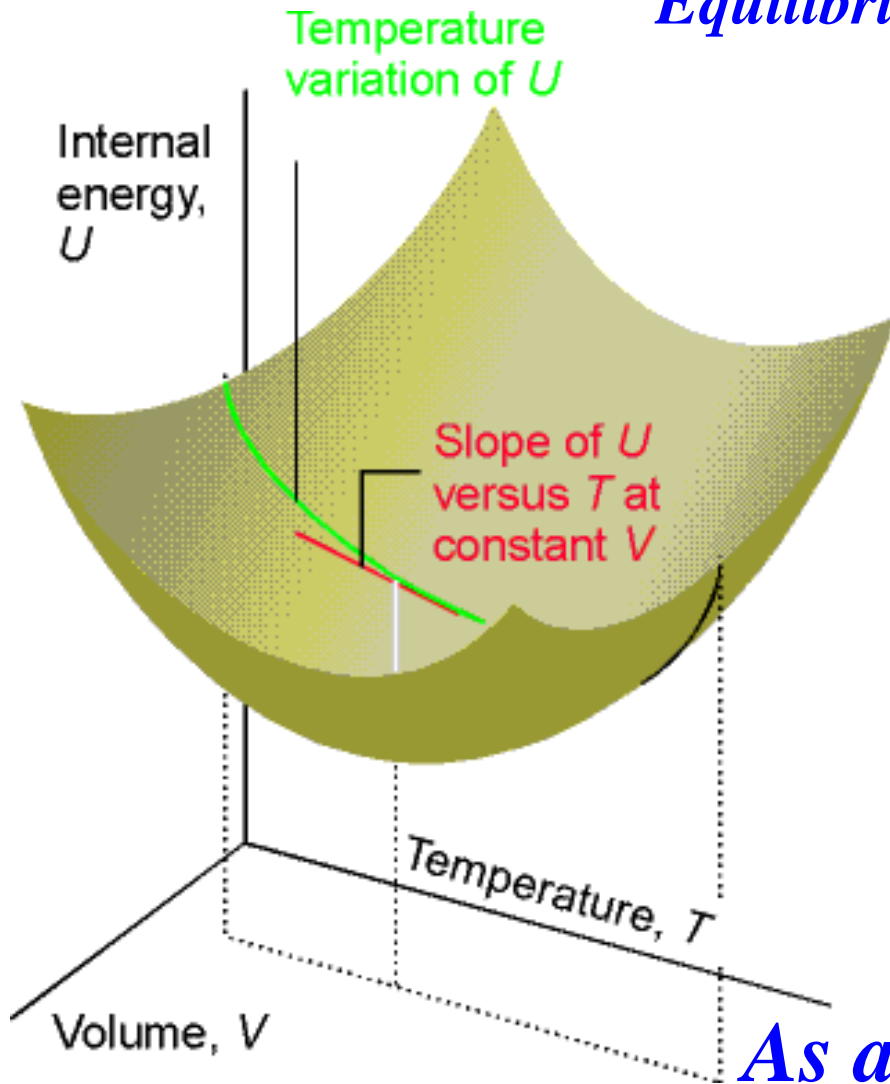


Fig. 2A.10

The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface.

The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to T .

The slope of this curve at any point is the **partial derivative** $(\partial U / \partial T)_V$.

As a function of two independent parameters

(1 Component)

2A.1. Work and Heat

Internal energy (S , L , or G) is stored in molecular bonds: in molecular **translation, rotation, and vibration**, and the energy of **mutual interactions** of molecules.

In molecular terms, the process of **heating** is the transfer of energy that makes use of the differences in **thermal motion** - the **random motion** of molecules - between the system and the surroundings.

Heat stimulates **random motion** (of either the system or the surroundings).

In molecular terms, **work** is the transfer of energy that makes use of **organized motion**. When a weight is raised or lowered, its atoms move in an organized way.

Drift Velocity:

The electrons moving with an electric field in an orderly direction.

Heat

Random Motion

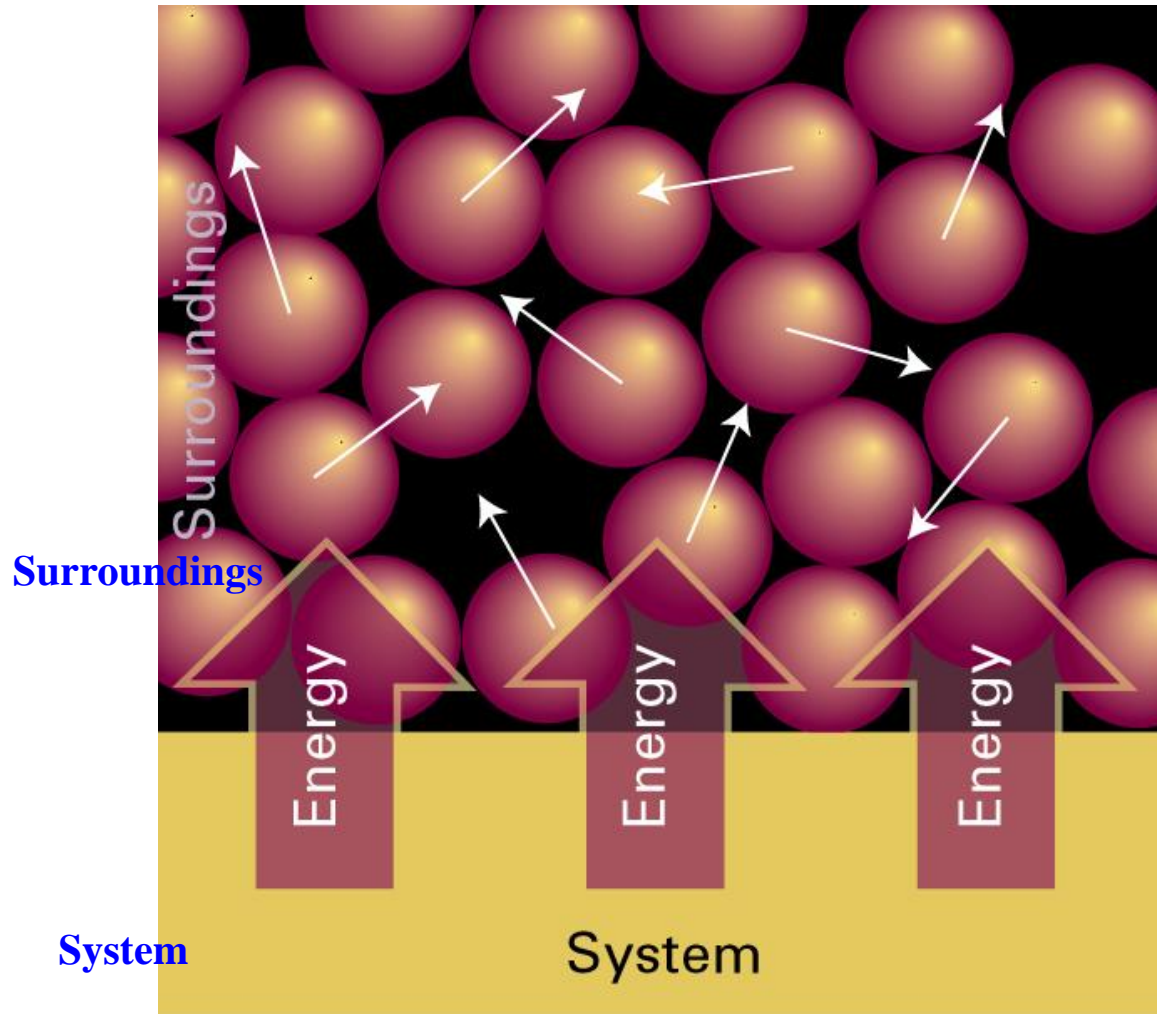


Figure 2A.3

When energy is transferred to the surroundings as heat, the transfer stimulates disordered motion of the atoms in the surroundings.

Transfer of energy from the surroundings to the system makes use of **disordered motion (thermal motion)** in the surroundings.

Movie: "Me Before You"

2B. Enthalpy

In many cases, it is more convenient to use temperature and pressure, rather than temperature and volume, as independent variables.

$$U(p, T)$$

$$dU(p, T) = \underbrace{\left(\frac{\partial U}{\partial T} \right)_p}_{\text{not heat capacity}} dT + \left(\frac{\partial U}{\partial p} \right)_T dp$$

not heat capacity

For me
For convenience

Define a new function called the Enthalpy H :

$$\underline{H \equiv U + pV}$$

$$\begin{aligned} H + dH &= (U + dU) + (p + dp)(V + dV) \\ &= U + dU + pV + Vdp + pdV + \cancel{dpdV} \end{aligned} \quad 0 (\because \text{doubly infinitesimal})$$

$$\begin{aligned}
 H + dH &= U + pV + dU + Vdp + pdV \\
 &= H + dU + Vdp + pdV
 \end{aligned}$$

$$\begin{aligned}
 dH &= dU + pdV + Vdp \\
 &= dU + d(pV)
 \end{aligned}$$

(*)

$$dU = dq - pdV \quad \text{Reversible or Irreversible (The First Law)} \quad (**)$$

By combining eqs (*) and (**), one obtains

$$\begin{aligned}
 \underline{dH} &= dq - pdV + pdV + Vdp \\
 &= \underline{dq + Vdp}
 \end{aligned}$$

Reversible or Irreversible

Now impose the condition that pressure is kept constant, *Experimentalist*

$$(dH)_p = (dq)_p$$

The increase in the property H is equal to the amount of heat added to a system at constant pressure.

$$\underline{\therefore C_p = \left(\frac{\partial q}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p}$$

2B.2. Calculation of $C_p - C_v$

$$H = U + pV$$

$$C_p - C_v = \left(\frac{\partial V}{\partial T} \right)_p \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right]$$

(2B.9)

General (derivation)

$$C_p - C_v = nR \quad \text{Ideal Gas}$$

Homework

$C_p - C_v = ?$

$C_p = \frac{dH}{dT}|_p = \frac{dU}{dT}|_p + p \frac{\partial V}{\partial T}|_p$

$C_p - C_v = \frac{\partial U}{\partial T}|_p + p \frac{\partial V}{\partial T}|_p - \frac{\partial U}{\partial T}|_v$

from $dU(V, T) = \frac{\partial U}{\partial V}|_T dV + \frac{\partial U}{\partial T}|_V dT$

$C_p - C_v = \frac{\partial U}{\partial V}|_T \frac{\partial V}{\partial T}|_p + \frac{\partial U}{\partial T}|_V + p \frac{\partial V}{\partial T}|_p - \frac{\partial U}{\partial T}|_V$

$= \frac{\partial V}{\partial T}|_p \left[p + \frac{\partial U}{\partial V}|_T \right]$

$\therefore \frac{U}{N} = \frac{3}{2} p T \quad C_p - C_v = R \quad \text{for ideal gas}$

$H \equiv U + pV$
 ~~$dH = dU + p dV$~~

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_p - C_V = \left(\frac{\partial V}{\partial T} \right)_p \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right]$$

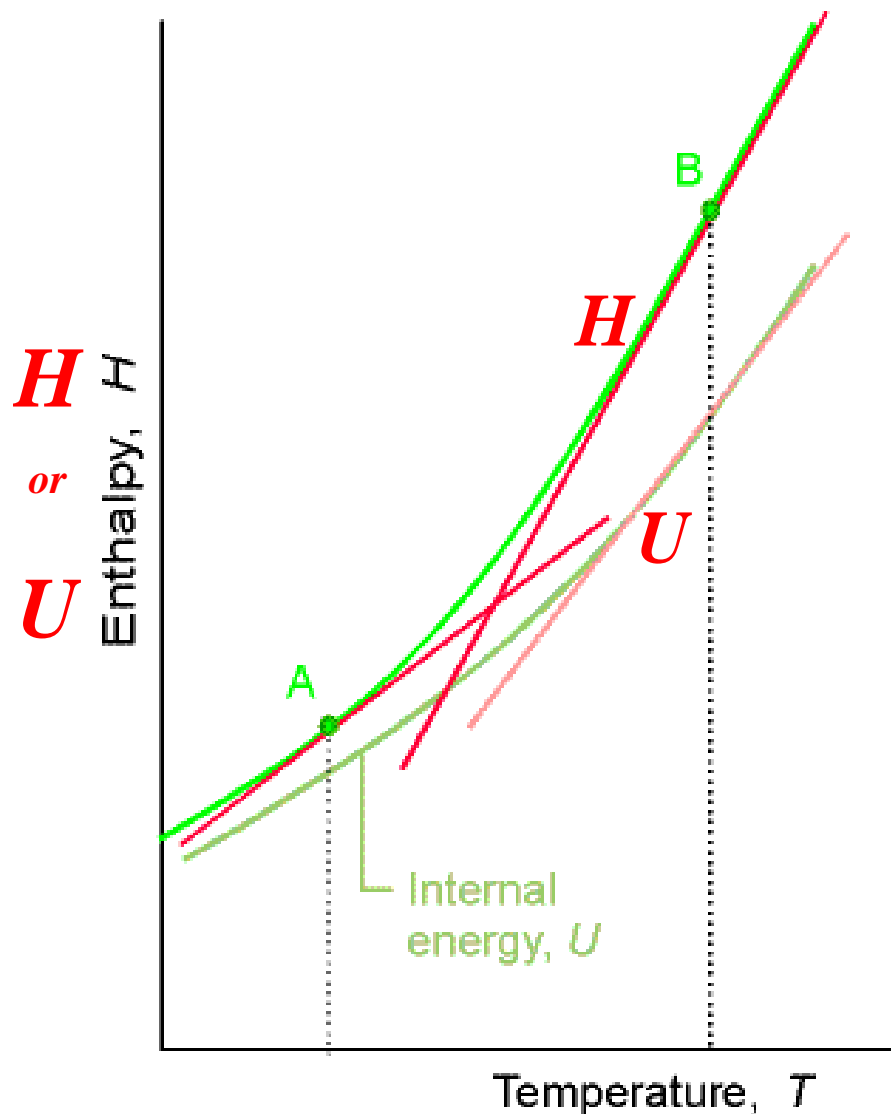


Figure 2B.3

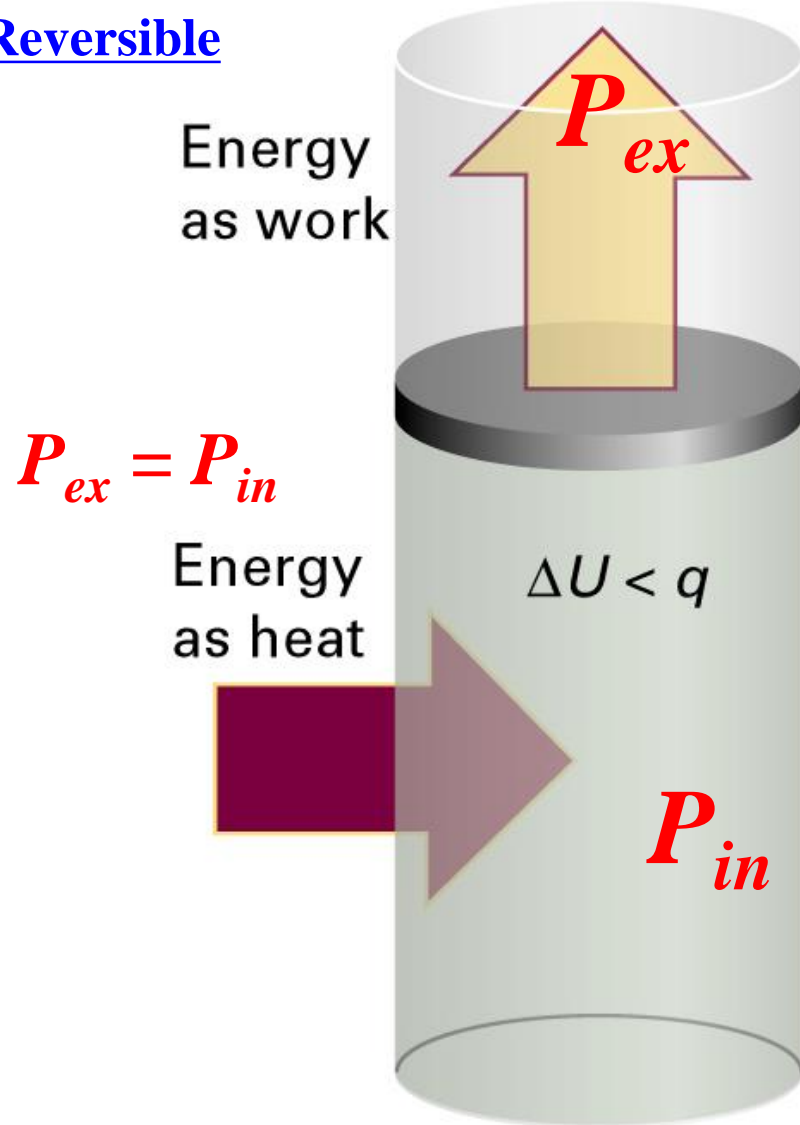
The slope of a graph of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity.

The slope of the graph may change with temperature, in which case the heat capacity may varies with temperature.

For gases, the slope of the graph of enthalpy vs. temperature is steeper than that of the graph of internal energy vs. temperature: C_p is larger than C_V .

[Positive Thermal-Expansion Coefficient]

Reversible



Weight Lifting from Thermal Expansion

Figure 2B.1

When a system is subjected to constant P and is free to change its volume by raising T , some of the energy supplied as heat may escape back into the surroundings as work.

In such a case, the change in internal energy is smaller than the energy supplied as heat.

$$C_p - C_V = nR \quad \text{Ideal Gas}$$

$$P V = N k_B T$$

$$P dV = N k_B dT$$

2E.1. Reversible Adiabatic Expansion (Perfect Gas)

$$dq = 0$$

Equilibrium = Independent of Path = State Function

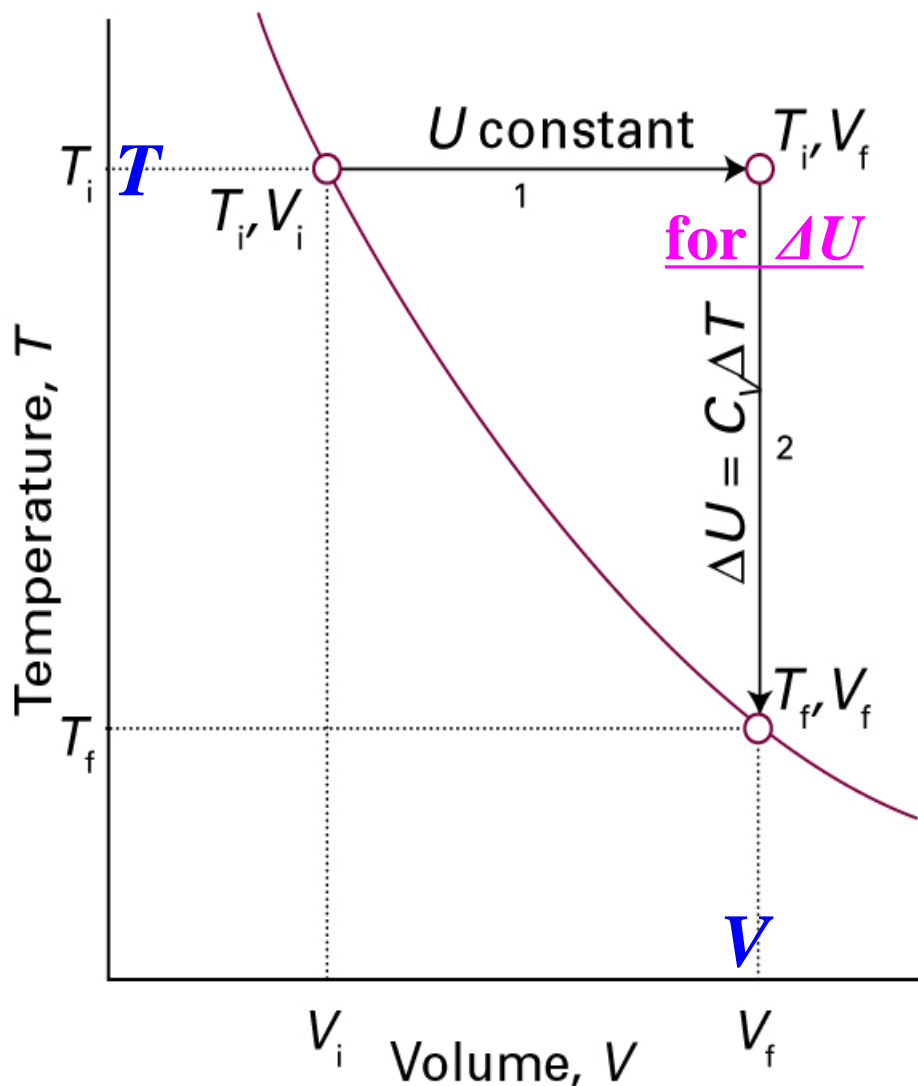


Figure 2E.1

To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps.

In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas.

In the second step, the temperature of the system is decreased at constant volume.

The overall change in internal energy is the sum of the changes for the two steps.

2E.1. Reversible Adiabatic Changes

Perfect Gas

The work of adiabatic change

$$T_i, V_i \rightarrow T_f, V_f$$

$$dU = dq + dw$$

$$dq = 0 \quad (\because \text{adiabatic})$$

$$C_V = (dU/dT)_V \quad \text{PPT 2-17}$$

$$\therefore dU = dw \quad \text{Through the adiabatic curve}$$

$$\therefore W = \int_{\text{initial state}}^{\text{final state}} (dU)_V = \int_{T_i}^{T_f} C_V dT_V = C_V (T_f - T_i)_V = C_V \Delta T_V$$

Through the path 1 and path 2

Note that U is dependent only on the temperature for ideal gas.

$$U(T)/N = \frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle$$

Derived from Maxwell-Boltzmann distribution

PPT 1-21

PPT 1-14

$$C_V/N = 3/2 k_B \quad 27$$

$$p_{ex} \approx p_{in}$$

$$dU = dq + dw$$

2E.1. Reversible Adiabatic Expansion of a Perfect Gas

$$dq = 0$$

$$\therefore dU = dw = -pdV$$

$$dU = C_V dT$$

Combining the two equations,

$$\underline{C_V dT = -pdV}$$

$U(T)$ = Perfect Gas

$$C_V/N = 3/2 k_B$$

$U(T,V)$ or $U(T,P)$ = Real Gas

$$C \equiv \frac{dQ}{dT}$$

On inserting $pV = nRT$, the last equality becomes

$$C_V dT = -\frac{nRT}{V} dV$$

$$C_V \frac{dT}{T} = -nR \frac{dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

$$\text{Let } c = \frac{C_V}{nR} = \frac{C_{V,m}}{R}$$

$$\left(\frac{T_f}{T_i} \right)^c = \left(\frac{V_i}{V_f} \right)$$

$$U(T)/N = 3/2 k_B T$$

$$C_V/N = 3/2 k_B$$

$c = 3/2$ for monoatomic ideal gas

(Ideal + Adiabatic + Reversible)

(2E.2b)

$$V_f T_f^c = V_i T_i^c \quad (2E.2b)$$

We can predict the temperature of a gas that has expanded adiabatically and reversibly from a volume V_i and temperature T_i to a volume V_f .

$$T_f = \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}} T_i \quad (\text{Ideal + Adiabatic + Reversible})$$

The work done on the ideal gas as it expands adiabatically and reversibly from V_i to V_f becomes:

$$\begin{aligned} \Delta U = w = C_v \Delta T &= C_v (T_f - T_i) = C_v \left[\left(\frac{V_i}{V_f} \right)^{\frac{1}{c}} T_i - T_i \right] \\ &= C_v T_i \left\{ \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}} - 1 \right\} \end{aligned} \quad (\text{Ideal + Adiabatic + Reversible})$$

2E.2. P - V Relation for Perfect Gas (Adiabatic Changes)

Calculation: Justif. 2E.2

[Homework]

Defining $\gamma = \frac{C_p}{C_v}$, we obtain

$$\underline{pV^\gamma = \text{constant}}$$

$$\gamma = 5/3$$

for monoatomic ideal gas

(Ideal + Adiabatic + Reversible)

$$p_f V_f^\gamma = p_i V_i^\gamma$$

$$w = C_V T_i \left\{ \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}} - 1 \right\}, \frac{1}{c} = \gamma - 1$$

$$c = \frac{C_{V,m}}{R}$$

$$\frac{1}{c} = \frac{R}{C_{V,m}} = \frac{C_{p,m} - C_{V,m}}{C_{V,m}}$$

$$= \frac{C_{p,m}}{C_{V,m}} - 1 = \gamma - 1$$

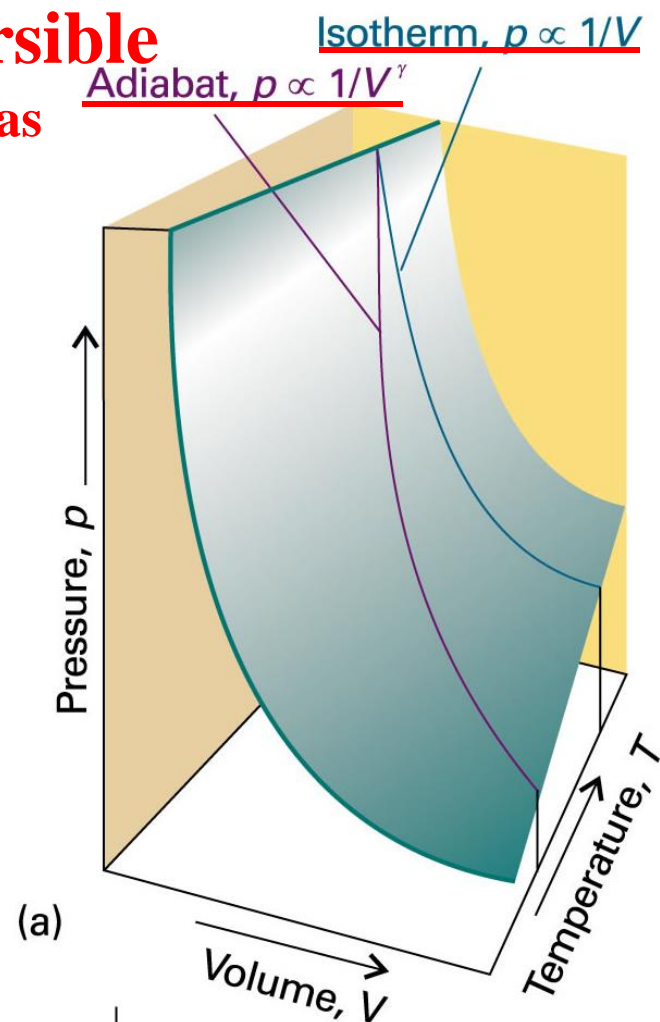
Combining the above two equations,

$$w = C_V T_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right\}$$

Since $\gamma > 1$ for all gases, the pressure p falls off faster with volume ($p \propto \frac{1}{V^\gamma}$: the curve is called an **adiabat**) than in the case of isothermal expansion ($p \propto \frac{1}{V}$).

Reversible

Ideal Gas



$$\gamma = \frac{C_p}{C_v} = 5/3$$

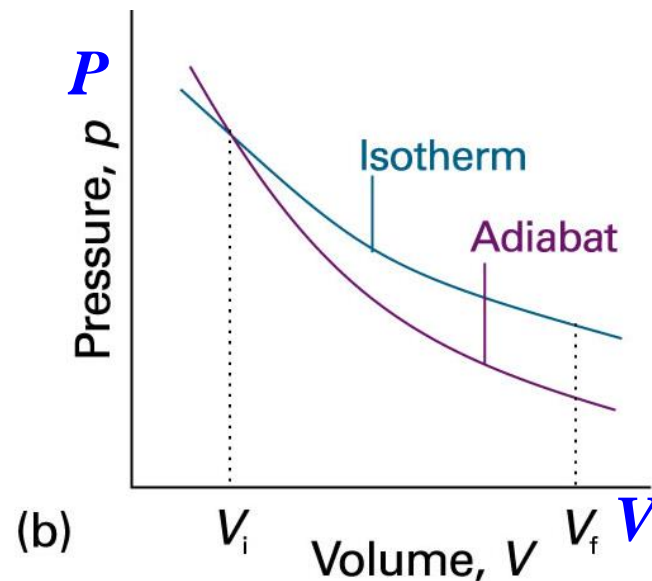


Figure 2E.2 An adiabat depicts the variation of pressure with volume when a gas expands **reversibly** and adiabatically.

(a) An adiabat for a perfect gas.

(b) Note that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature decreases in the former.

Molecular Interpretation of Internal Energy (Ideal Gas)

Consider the case of **a monatomic gas** at a temperature T . We know that the kinetic energy of one atom of mass m is

$$E_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \quad (\text{A})$$

According to **the equipartition theorem**, the average energy of each term is $\frac{1}{2}kT$, where k is the Boltzmann constant. Therefore, the mean energy of the atoms is $\frac{3}{2}kT$ and the total energy of the gas (there being no potential energy contribution) is $\frac{3}{2}NkT$, or $\frac{3}{2}nRT$. We can therefore write

$$U_m = U_m(0) + \frac{3}{2}RT \quad \text{Monatomic Gas (B)}$$

where $U_m(0)$ is the molar internal energy at $T = 0$ K, when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of atoms. This equation shows that **the internal energy of a perfect gas** increases linearly with temperature.

(Only in Classical Physics)

Since the heat capacity at constant volume is:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (C)$$

the heat capacity of a monatomic perfect gas can be calculated by inserting the equation (B) into equation (C). That is,

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_m = \frac{3}{2} R \quad (D)$$

For a linear molecule, we must consider rotational contributions in addition to translational contributions. Linear molecule has two rotational modes of motion, each contributing a term $\frac{1}{2}kT$ to the internal energy.

$$U_m(T) = U_m(0) + \frac{5}{2} RT$$

Chap. 0

Quantized Energy Level

Fig. A.2

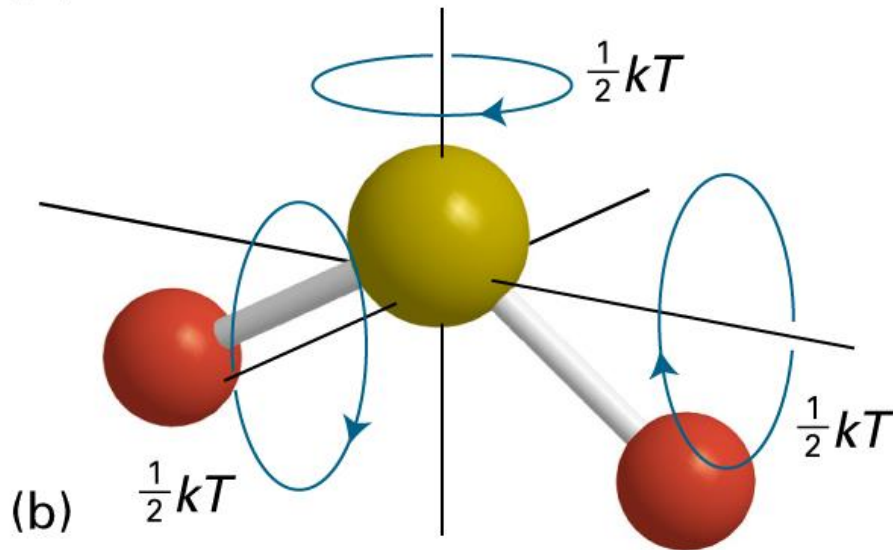
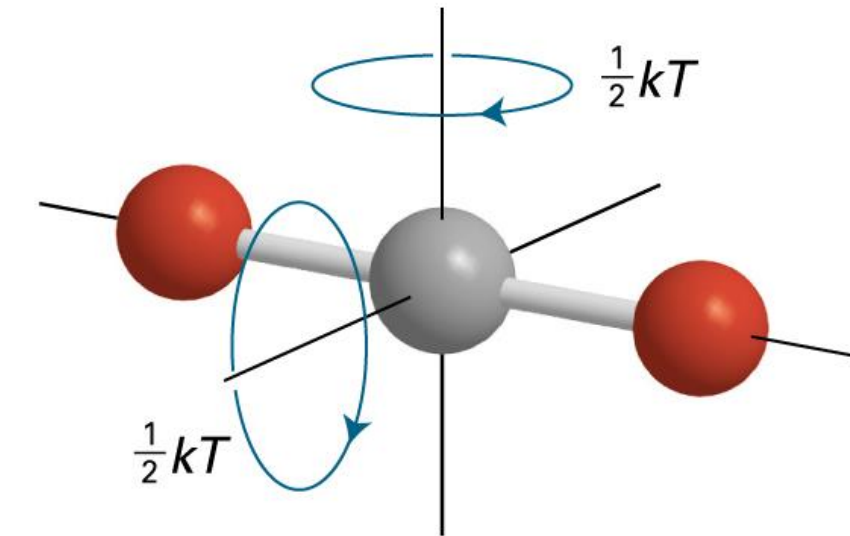
Translation < Rotation < Vibration < Electronic

Fig. B.3

Equipartition Theorem

$$U_m(T) = U_m(0) + \frac{5}{2}RT$$

Fig. A.2 A non-linear molecule can rotate around three axes and therefore the mean rotational energy is $\frac{3}{2}kT$, and there is a rotational contribution of $\frac{3}{2}RT$ to the molar internal energy.



$$U_m(T) = U_m(0) + 3RT$$

(Only in Classical Physics)

For any kind of expansion of any kind of material, the work done on the system as it changes from V_i to V_f is given by:

$$w = -\int_{V_i}^{V_f} p_{ex} dV \quad \text{Reversible or Irreversible}$$

where P_{ex} , the external pressure, depends upon how the change is organized.

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

(Ideal Gas)

0 0 ideal gas
isothermal

Type of work	w	q	ΔU	ΔT
Expansion against $p = 0$				
Isothermal	0	0°	0°	0
Adiabatic	0	0	0	0
Expansion against constant pressure				
Isothermal	$-p_{ex}\Delta V$	$p_{ex}\Delta V^\circ$	0°	0
Adiabatic	$-p_{ex}\Delta V$	0	$-p_{ex}\Delta V$	$\frac{-p_{ex}\Delta V^\circ}{C_V}$
Reversible expansion or compression				
Isothermal	$-nRT \ln \frac{V_f^\circ}{V_i}$	$nRT \ln \frac{V_f^\circ}{V_i}$	0°	0
Adiabatic	$C_V\Delta T^\circ$	0	$C_V\Delta T^\circ$	$T_i \left\{ \left(\frac{V_i}{V_f} \right)^{1/c} - 1 \right\}^\circ$

† The entries marked $^\circ$ are for a perfect gas; the rest apply to any substance. $c = C_V/R$.

2C. Thermochemistry

ΔH : + or -

Thermochemistry: the study of the heat produced or required for the chemical reaction

Reaction enthalpy $\Delta U = \Delta Q_V, \quad \Delta H = \Delta Q_p$

Reactant (Equilibrium/Metastable) + ΔH \rightarrow Product (Equilibrium /Metastable)

2C.1. Standard Enthalpy Changes

Absolute enthalpies of substances are meaningless. Still, enthalpies relative to an arbitrary standard state may be used, provided the same standard state is used for the reactants and products.

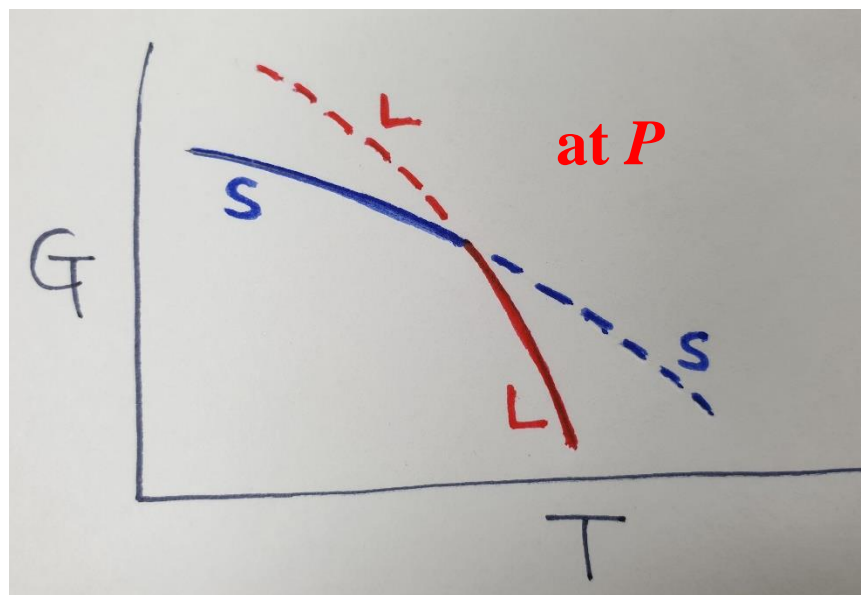
The standard enthalpy change, ΔH° : the change in enthalpy for a process in which the initial and final substances are in their standard states. Here, the standard state of some substance is its most stable form under 1 bar ($\approx atm$) and at the temperature specified.

Example of standard Enthalpy Change

standard enthalpy of Vaporization



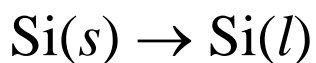
$$\Delta H_{\text{vap}}^{\circ}(373\text{K}) = +40.66\text{kJ/mol}$$



Enthalpies of physical changes

1. Standard enthalpy of Vaporization

2. Standard enthalpy of Fusion



$$\Delta H_{\text{fus}}^{\circ}(273\text{K}) \approx +50\text{kJ/mol}$$

~0.5 eV/atom

3. Standard enthalpy of Sublimation

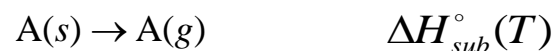


$$\Delta H_{\text{sub}}^{\circ}(298\text{K}) = +716.69\text{kJ/mol}$$

Diamond?

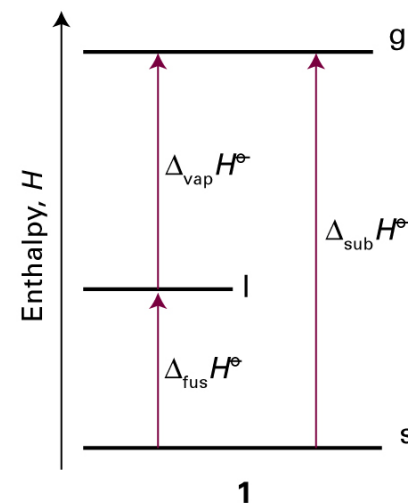
Reactant (Equilibrium/Metastable) + $\Delta H \rightarrow$ Product (Equilibrium/Metastable)

A change in **enthalpy** is independent of the path between the two states:



overall: $A(s) \rightarrow A(g)$

$$\therefore \Delta H_{sub}^{\circ}(T) = \Delta H_{fus}^{\circ}(T) + \Delta H_{vap}^{\circ}(T)$$



A consequence of **H** being a state function is that the standard enthalpy of a forward process and its reverse must be equal and opposite:

$$\Delta H^{\circ}(\text{reverse}) = -\Delta H^{\circ}(\text{forward})$$

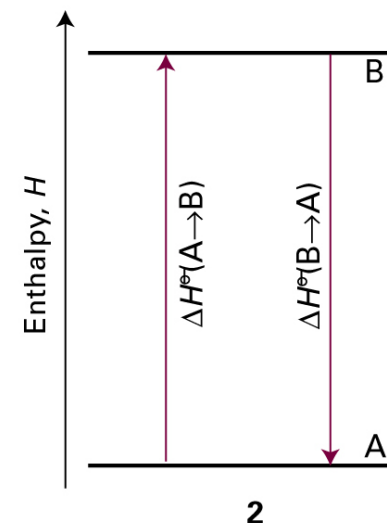
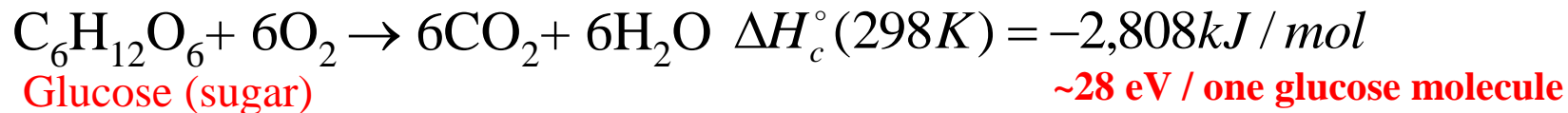


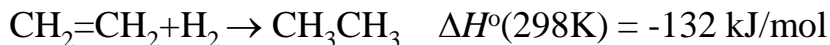
Fig. 2C.1

2C.1(b). Enthalpies of Chemical Changes

1. Standard enthalpy of combustion (oxidation)



2. Enthalpy of hydrogenation



$$|-246| < |-3 \times 132|$$

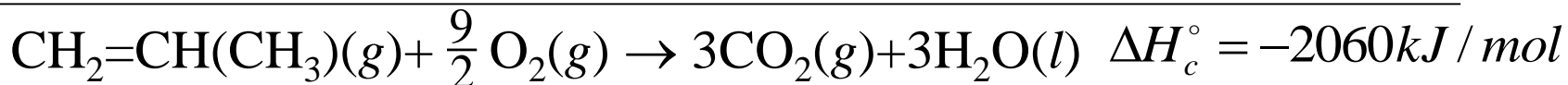
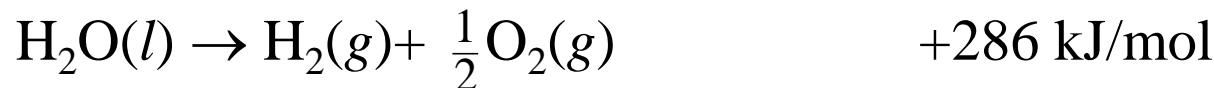
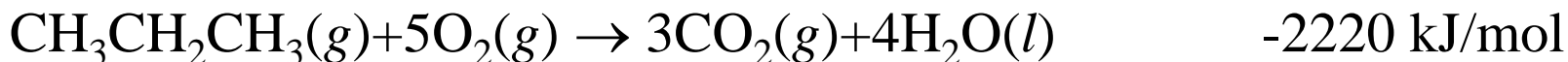
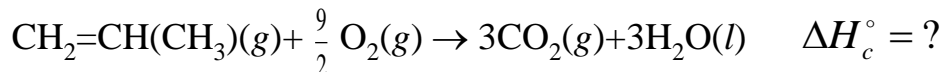
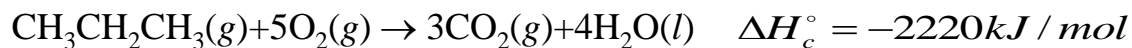
Why is the enthalpy of hydrogenation of benzene is less than the value of three times of enthalpy of hydrogenation of ethylene?

Because of resonance stabilization of benzene.

Reactant (Equilibrium/Metastable) + $\Delta H \rightarrow$ Product (Equilibrium /Metastable)

2C.1(c). Hess's Law

The enthalpy change of any reaction may be expressed as the sum of the enthalpy changes of a series of reactions into which the overall reaction may formally be divided.



$H(T, P, N_j)$: State Function
Reversible

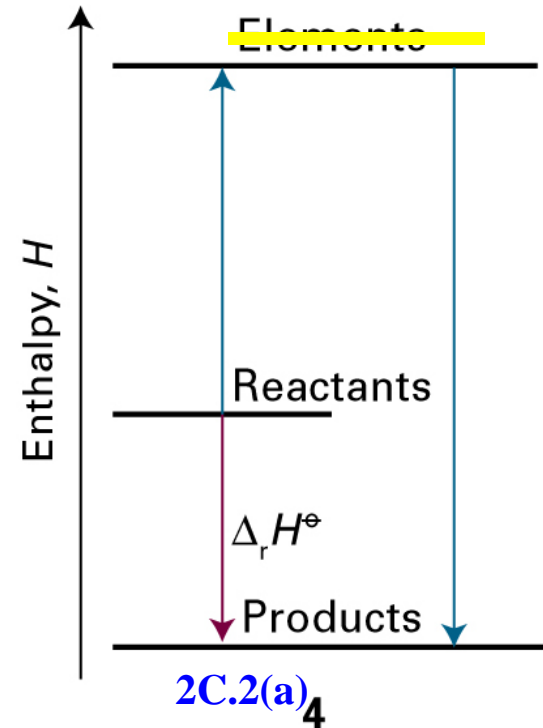
2C.2(a). Enthalpy of Formation

The standard enthalpy of formation ΔH_f° of a substance is the standard reaction enthalpy for its formation from elements in their reference states.

It is convenient to adopt the convention that the enthalpy of every element in its standard state is zero.

The reaction can be regarded as proceeding by decomposing the reactants into elements and then forming those elements into products.

Reference Point



Cohesive Energy = *Energy required to form separated neutral atoms in their ground state from the solid (at 0 K at 1 atm)*

$$\text{Si}(s) = 4.6 \text{ eV/atom}$$

Charles Kittel

“Introduction to Solid State Physics”

Cohesive Energy \approx Enthalpy of Sublimation

2C.3. The Variation of Enthalpy with Temperature

$$\underline{C_p = \left(\frac{\partial H}{\partial T} \right)_p} \quad dH = C_p dT$$

$$C_p = C_p(T)$$

$$dH = C_p(T) dT$$

$$\underline{\therefore H(T_f) - H(T_i) = \int_{T_i}^{T_f} C_p(T) dT}$$

*Reversible =
Time Independent*

This expression applies to every species involved in the reaction, and so the reaction enthalpies at T_f and T_i are related by **the Kirchhoff's Law**:

$$\underline{\Delta H = H(\text{prod.}) - H(\text{react.})}$$

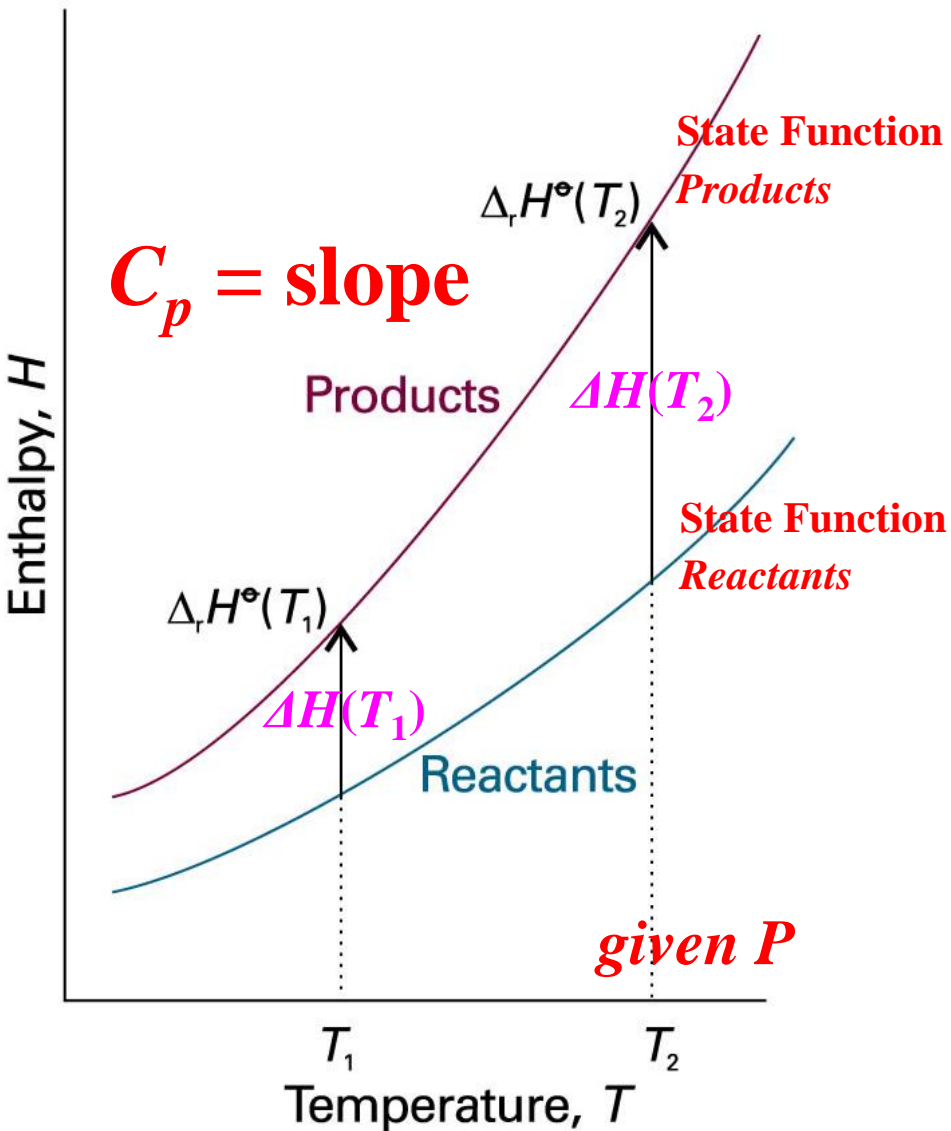


Figure 2C.2

An illustration of the content of **Kirchhoff's law**.

When the temperature increases, the enthalpies of the products and the reactants both increase, but may do so to different extents.

In each case, the change in enthalpy depends on the heat capacities of the substances.

The change in reaction enthalpy reflects the difference in the heat capacities.

$$\underline{\Delta H = H(\text{product}) - H(\text{reactant})}$$

The Relation between ΔH and ΔU

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + [pV](\text{prod}) - [pV](\text{react})$$

For liquids and solids:

$$[pV](\text{prod}) - [pV](\text{react}) \approx 0.$$

$$\underline{\therefore \Delta H \approx \Delta U}$$

even at MIT

In the case of reactions involving gases, assuming that the gas behaves as an ideal gas, $pV=nRT$.

$$\begin{aligned}\Delta H &= \Delta U + pV(\text{prod}) - pV(\text{react}) \\ &= \Delta U + nRT(\text{prod}) - nRT(\text{react})\end{aligned}$$

$$\text{Since } \Delta n_{\text{gas}} = n_{\text{gas}}(\text{prod}) - n_{\text{gas}}(\text{react})$$

$$\therefore \underline{\Delta H = \Delta U + \Delta n_{\text{gas}} RT}$$

Reactant
2 molecules

Product
1 molecule



2D. State Functions and Differentials

State Function: Properties that are determined only by the present state of the system, and are independent of how that state has been prepared.

e.g., internal energy, volume, pressure, temperature, density, refractive index, etc. **In Equilibrium.**

Path Function: Properties that are related to what is happening to the system when the changes are in progress.

e.g., work, heat, etc.

2D.1. Exact and Inexact Differentials

U, V : state function

$$\int_a^b dU = U_b - U_a$$

Since the integral is path independent, the differential of a state function is called an exact differential.

q, w : path function

The integrals of their differentials in going from state a to b depend upon the path chosen. Therefore, their differentials are called inexact differentials.

$$\int_a^b dw = w \neq w_b - w_a$$

$$\Delta U = \int_{U_i}^{U_f} dU = U_f - U_i$$

dU : complete or exact differential

$U(T, V)$

$U(T, P)$

or

$U(V, \varepsilon)$

1 component

$$q = \int_{path} dq$$

$d w$ or $d q$: incomplete or inexact differential

1. q is not a state function, and the heat added cannot be expressed in the form of $q_f - q_i$.
2. The path of integration should be specified because q depends on the path selected.

Example 2D.1 (Ideal Gas)

$T_i, V_i \rightarrow T_f, V_f$: Expansion of an ideal gas isothermally

1. Path 1: Free expansion against zero external pressure.
2. Path 2: Reversible, isothermal expansion accompanied by the appropriate influx of heat. $T_{ex} = T_{in}$ $P_{ex} = P_{in}$

Find w , q and dU for each path.

Homework

Solution:

$$(path\ 1) \quad w = -p\Delta V = 0$$

$$(path\ 2) \quad w = -\int_{V_i}^{V_f} p dV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \ln \frac{V_f}{V_i}$$

PPT 2-15

$$dU=0 \text{ for an expansion of an ideal gas } (T_i = T_f) \quad \because \left(\frac{\partial U}{\partial V} \right)_T = 0$$

$$(path\ 1) \quad q = 0 \quad (\because q = -w)$$

$$(path\ 2) \quad q = nRT \ln \frac{V_f}{V_i}$$

$U(T, V)$ or $U(T, P)$

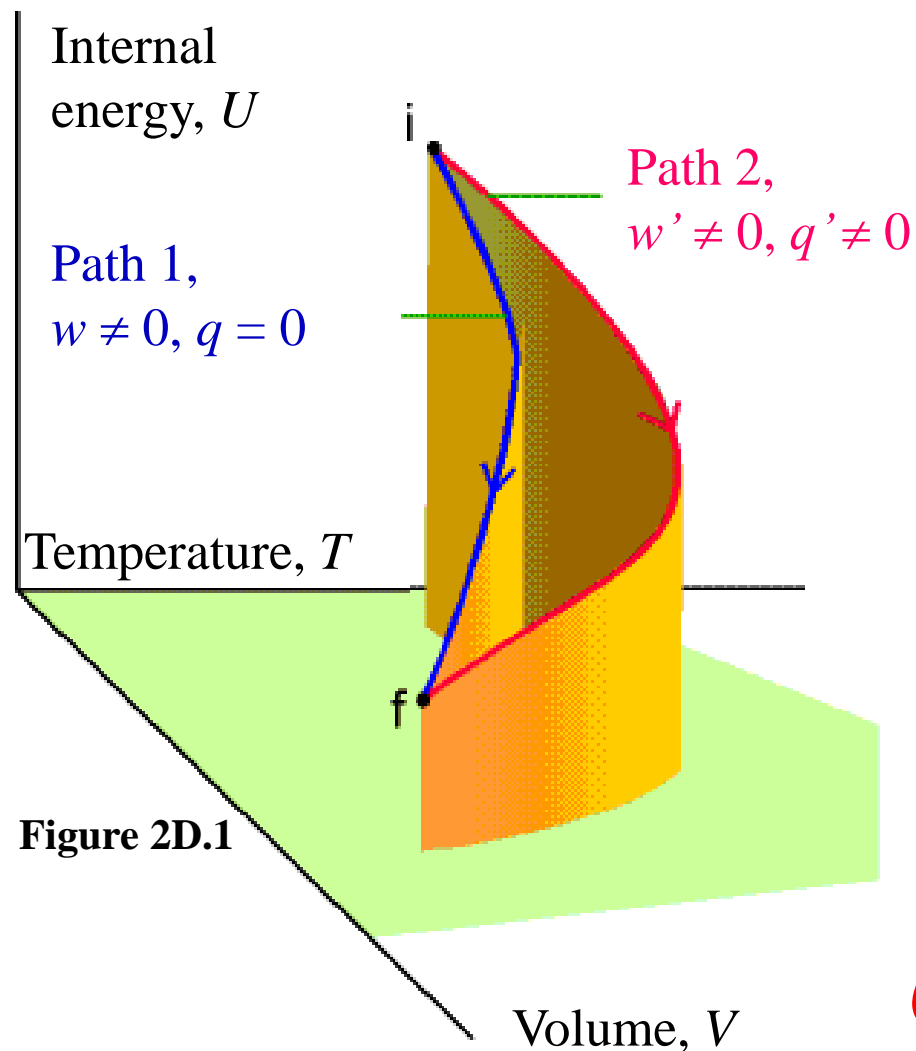


Figure 2D.1

As the volume and temperature of a system change, the internal energy changes.

An adiabatic and a non-adiabatic path are shown as path 1 and 2, respectively:

They correspond to different values of q and w , but to the same value of ΔU .

$$dU = \delta q + \delta w$$

The sum of two inexact differentials can be an exact differential.

2D.2. Changes in Internal Energy U : State Function

$$U = U(V, T)$$


$$U(V + dV, T) = U(V, T) + \left(\frac{\partial U}{\partial V} \right)_T dV$$


$$U(V, T + dT) = U(V, T) + \left(\frac{\partial U}{\partial T} \right)_V dT$$

$$U(V + dV, T + dT) = U(V, T) + \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

The internal energy at $(V + dV, T + dT)$ differs from that at (V, T) by an infinitesimal amount, which we write dU .

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



 The change of the internal energy as the volume of the system is changed isothermally

$$\left(\frac{\partial U}{\partial V} \right)_T \equiv \Pi_T$$

Definition of 'internal pressure'

(2D.4)

Manipulating the First Law

$$dU = dq + dw \quad U = U(V, T)$$

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

$$\underline{H \equiv U + pV} \quad H = H(T, p)$$

$$dH = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dP$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$\underline{dU(T, V) = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV}$$

$$\underline{dH(T, P) = C_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp}$$

State function
Exact differential (2D.3)

(2D.13)

How the Internal Energy Varies with Volume

$$\left(\frac{\partial U}{\partial V}\right)_T \equiv \Pi_T$$

Definition of
'internal pressure'

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_p = C_V + \left(\frac{\partial U}{\partial V}\right)_T \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}$$

the rate of change of volume with
the increase of temperature

$$\alpha = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p \quad \text{\underline{\textbf{The isobaric thermal-expansion coefficient}}} \quad \text{\textbf{(2D.6)}}$$

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \alpha V \left(\frac{\partial U}{\partial V}\right)_T \quad \text{\textbf{(2D.3)}}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = ?$$

How the Internal Energy Varies with Volume

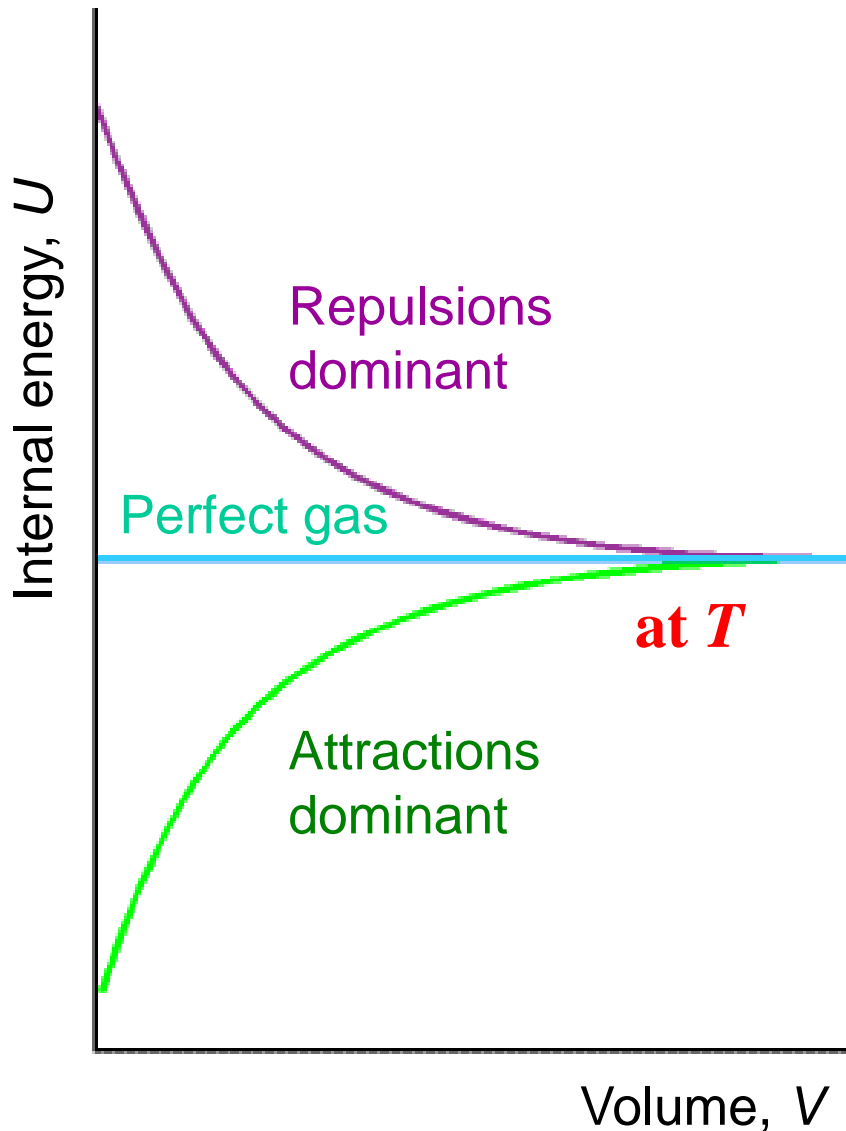
$$\left(\frac{\partial U}{\partial V}\right)_T = \Pi_T \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$\left(\frac{\partial U}{\partial V}\right)_T$ is a measure of how the interactions change when the volume of the sample is changed isothermally.

This is supported by noting that the case of a van der Waals gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \quad (\text{calculation on ppt 2-59})$$

We expect that the coefficient is smaller for gases than for solids because we know that molecular interactions are not very important in gases.



$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \quad \text{in van der Waals gas}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \Pi_T \quad \text{Definition of 'internal pressure'}$$

Figure 2D.4

For a perfect gas, the internal energy is independent of the volume (at constant temperature).

If attractions are dominant in a real gas, the internal energy increases with volume because the molecules become further apart on average.

If repulsions are dominant, the internal energy decreases as the gas expands.

(skip)

$$dU = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Thermometer

$$dU = \delta q + \delta w$$

(skip)

Joule Experiment

$$w = 0 \text{ (expansion into the vacuum)}$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad \text{Perfect Gas}$$

$$\Delta U = 0$$

$$q = 0 \text{ (good insulator)}$$

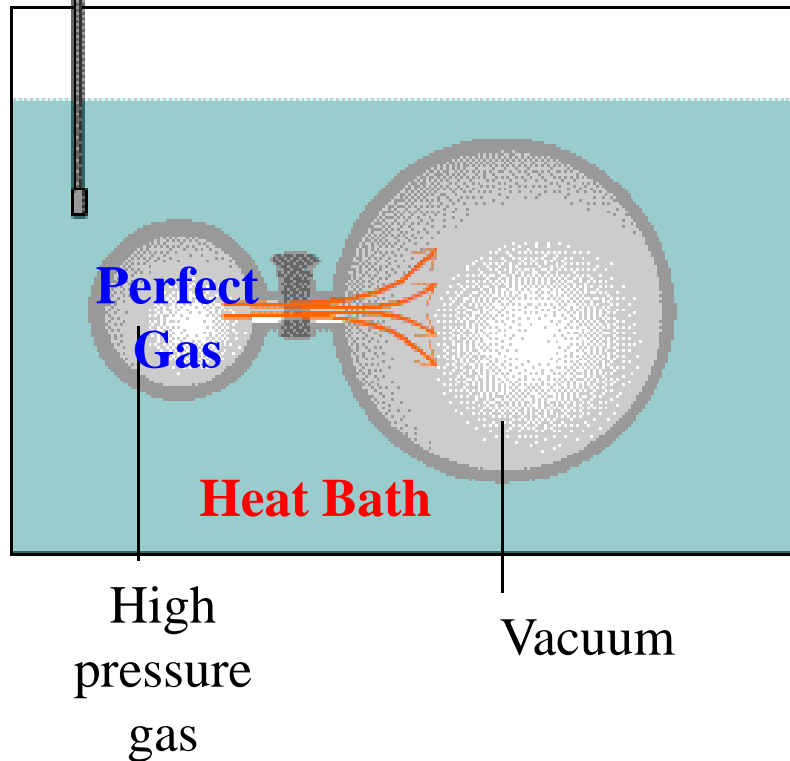


Figure 2D.5

A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands into a vacuum.

The heat absorbed by the gas is proportional to the change in temperature of the bath.

He has observed no change in temperature.

Problem:

Heat capacity of the apparatus is huge.

Definition of
'internal pressure' $\left(\frac{\partial U}{\partial V}\right)_T = \Pi_T$

Homework:

Will be proved in Chap. 3.

Use equation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ to prove that $\left(\frac{\partial U}{\partial V}\right)_T$ of an ideal gas is zero: that is, evaluate the right-hand side using $p = \frac{nRT}{V}$.

Evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ for the van der Waals equation.

Solution:

For an ideal gas, $\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T \frac{nR}{V} - p = p - p = 0$$

van der Waals Gas

Homework

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m - b} \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{RT}{V_m - b} - p = \frac{RT}{V_m - b} - \frac{RT}{V_m - b} + \frac{a}{V_m^2} = \frac{a}{V_m^2}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2} \quad \text{Definition of 'internal pressure'}$$

The van der Waals constant a is directly related to the attractive forces between the molecules, as is the internal pressure.

-Wed/Mar/23/22

Note: Relations between partial derivatives

If f is a function of x and y , then when x and y change by dx and dy , f changes by

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

Partial derivatives may be taken in any order:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

In the following, z is a variable on which x and y depend (for example, x , y , and z might correspond to p , V , and T).

Relation No. 1. When x is changed at constant z :

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

Relation No. 2 (the Inverter).

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

Relation No. 3 (the Permuter).

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

By combining this and Relation No. 2 we obtain Euler's chain relation:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Relation No. 4. This relation establishes whether or not df is an exact differential.

$$df = g dx + h dy \text{ is exact if } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

If df is exact, its integral between specified limits is independent of the path.

2D.3. Temperature Dependence of Enthalpy

State Function

Exact differential

(2D.13)
ppt 2-53

$$dH(T, P) = C_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

$$\left(\frac{\partial H}{\partial T} \right)_V = C_p + \left(\frac{\partial H}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V$$

$$\left(\frac{\partial p}{\partial T} \right)_V = - \frac{1}{\left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T} = - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T}$$

Thermal-Expansion Coefficient

the change of volume under the influence of pressure at constant temperature

Isothermal Compressibility

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

Negative sign, because κ is convenient positively.

(2D.7)

Bulk Modulus = κ^{-1}

diamond

2D.3. The Joule-Thompson Effect

$$\left(\frac{\partial H}{\partial T}\right)_V = C_p + \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

Thermal-Expansion Coefficient
Isothermal Compressibility

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = -\frac{\alpha V}{-\kappa V} = \frac{\alpha}{\kappa}$$

$$\therefore \left(\frac{\partial H}{\partial T}\right)_V = C_p + \left(\frac{\alpha}{\kappa}\right) \left(\frac{\partial H}{\partial p}\right)_T$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{\left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p} = -\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p$$

$$= -\left(\frac{\partial T}{\partial p}\right)_H C_p$$

How do you measure $\left(\frac{\partial T}{\partial p}\right)_H$?

(2D.13)

$$\left(\frac{\partial T}{\partial p} \right)_H ?$$

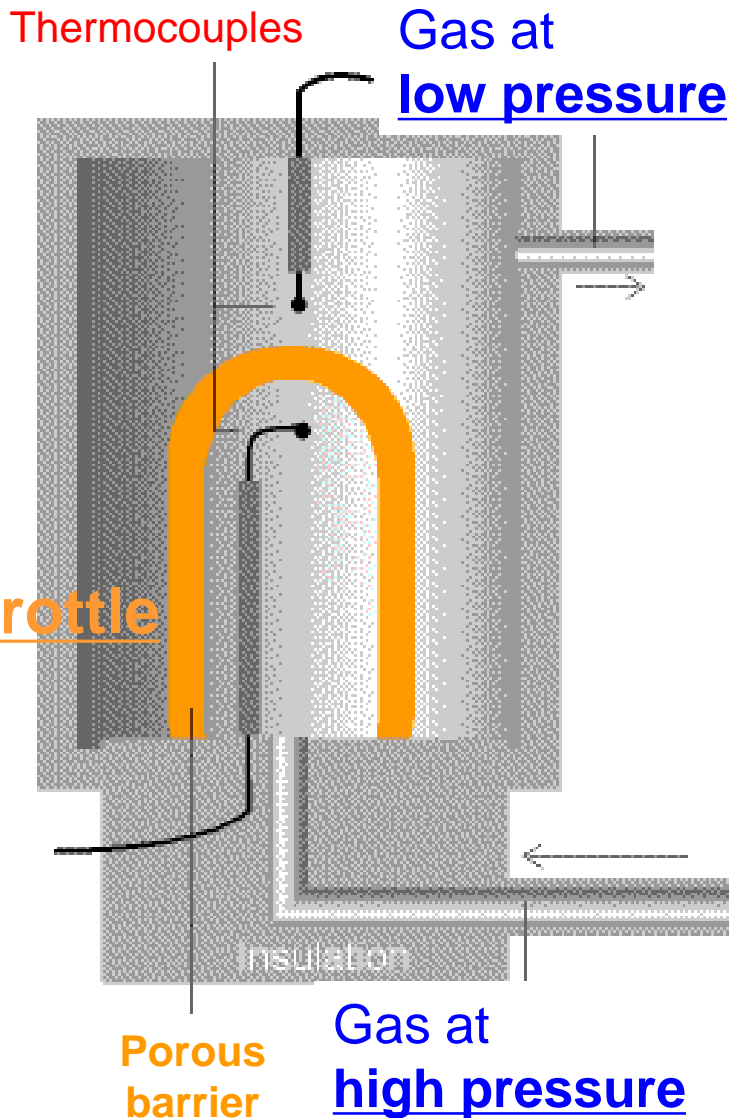
Figure 2D.6

A diagram of the apparatus used for measuring the Joule-Thomson effect.

The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated.

As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy)

Whether the expansion results in a heating or a cooling of the gas depends on the conditions.



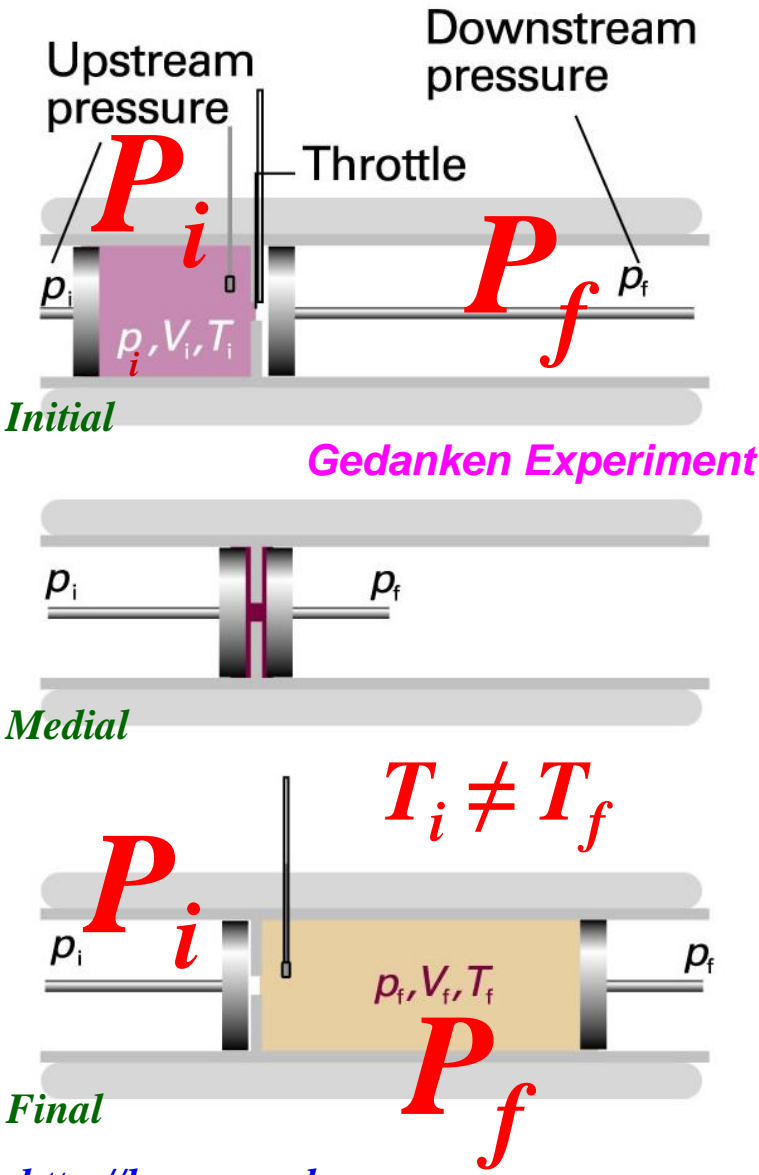
Thermally Insulated
(The Whole Setup)



$$\left(\frac{\partial T}{\partial p}\right)_H ?$$

Justification 2D.3 Joule-Thomson Effect

$$\Delta q = 0$$



~~isothermal~~ compression: the work done on the gas (left side) $= -p_i(0 - V_i) = p_i V_i$

~~isothermal~~ expansion: the work done on the gas (right side) $= -p_f(V_f - 0) = -p_f V_f$

the total work on the gas $= p_i V_i - p_f V_f$

\therefore the change in internal energy

$$U_f - U_i = p_i V_i - p_f V_f$$

\therefore $U_f + p_f V_f = U_i + p_i V_i$

$\therefore H_f = H_i$ (no change in enthalpy, **isenthalpic**)

Figure 2D.7 A diagram representing the thermodynamic basis of **Joule-Thomson expansion**. The pistons represent the upstream and downstream gases, which maintain **constant pressures** either side of the throttle. The transition from the top diagram to the bottom diagram, which represents the passage of a given amount of gas through the throttle, occurs without change of enthalpy.

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H : \text{Joule-Thompson coefficient} \quad \left(\frac{\partial T}{\partial p} \right)_H ? \quad (2D.14)$$

$\mu_{JT} > 0 = dp < 0 \rightarrow dT < 0 = \text{The gas cools on expansion.}$

(skip) $\mu_{JT} < 0$: if $dT > 0$ and $dp < 0$, the gas is heated by expansion.

Gases showing heating effects ($\mu_{JT} < 0$) show a cooling ($\mu_{JT} > 0$) effect when their temperature has been lowered beneath their inversion temperature.

Below its inversion temperature a gas is cooled on expansion. For a sufficiently large pressure drop, the cooling may drop the temperature below the boiling point of the gas, when the liquid will form. This principle is applied to making refrigerator.

$$\begin{aligned} \left(\frac{\partial H}{\partial p} \right)_T &= - \left(\frac{\partial T}{\partial p} \right)_H C_p = -\mu_{JT} C_p \\ \left(\frac{\partial H}{\partial T} \right)_V &= C_p + \left(\frac{\alpha}{\kappa} \right) \left(\frac{\partial H}{\partial p} \right)_T = C_p + \left(\frac{\alpha}{\kappa} \right) (-\mu_{JT} C_p) \\ &= \left(1 - \frac{\alpha \mu_{JT}}{\kappa} \right) C_p \end{aligned} \quad (2D.15)$$

Joule-Thomson Coefficient: μ_{JT}

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H$$

Joule-Thomson coefficient

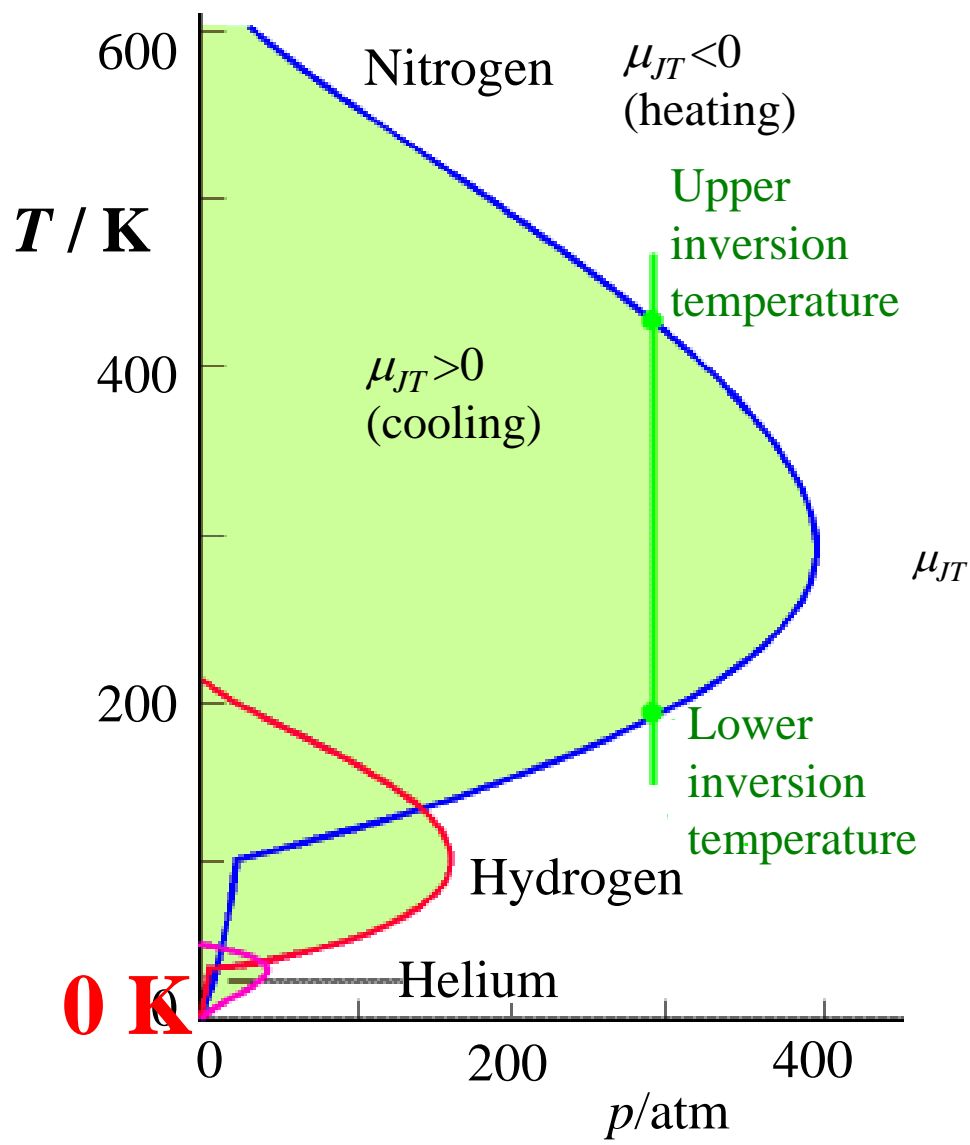


Figure 2D.11

The **inversion temperatures** for three real gases, nitrogen, hydrogen, and helium.

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H$$

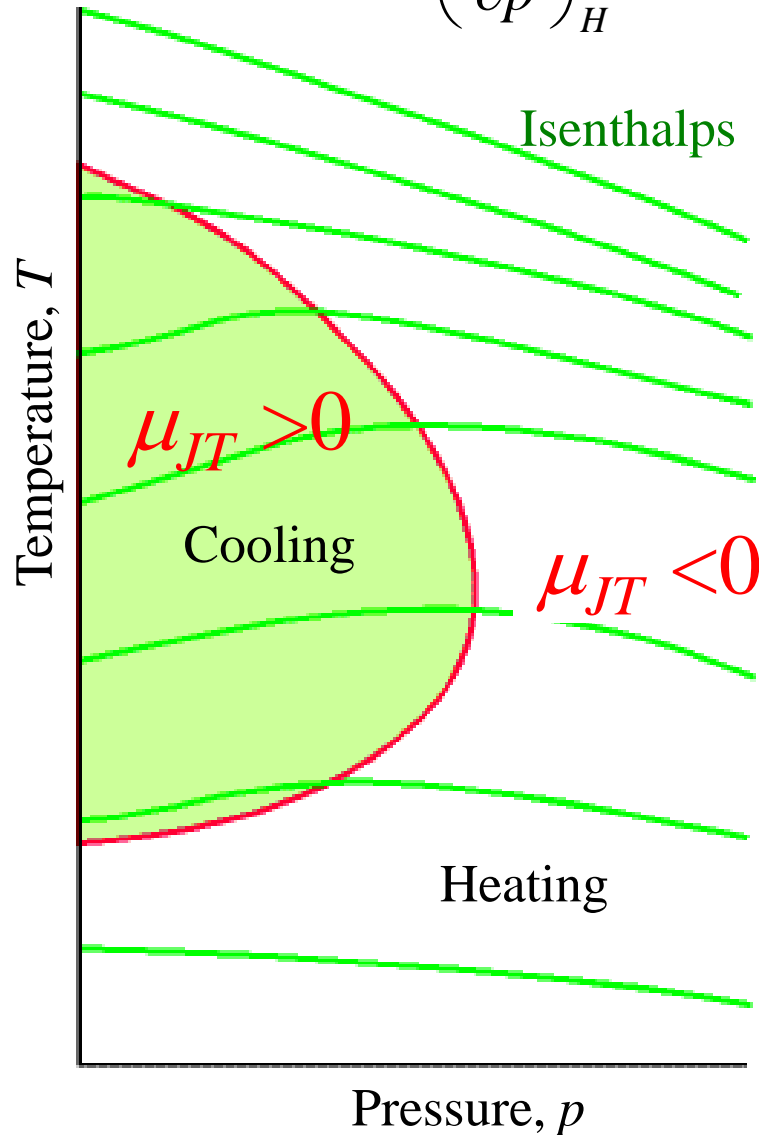


Figure 2D.10

The sign of the Joule-Thomson coefficient, μ_{JT} , depends on the conditions. Inside the boundary, the shaded area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the **inversion temperature** of the gas at that pressure.

For a given pressure, the temperature must be below a certain value if cooling is required. However, if it becomes too low, the boundary is crossed again and heating occurs.

Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy.

The inversion temperature curve runs through the points of the isenthalps where their slopes change from negative to positive.

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H$$

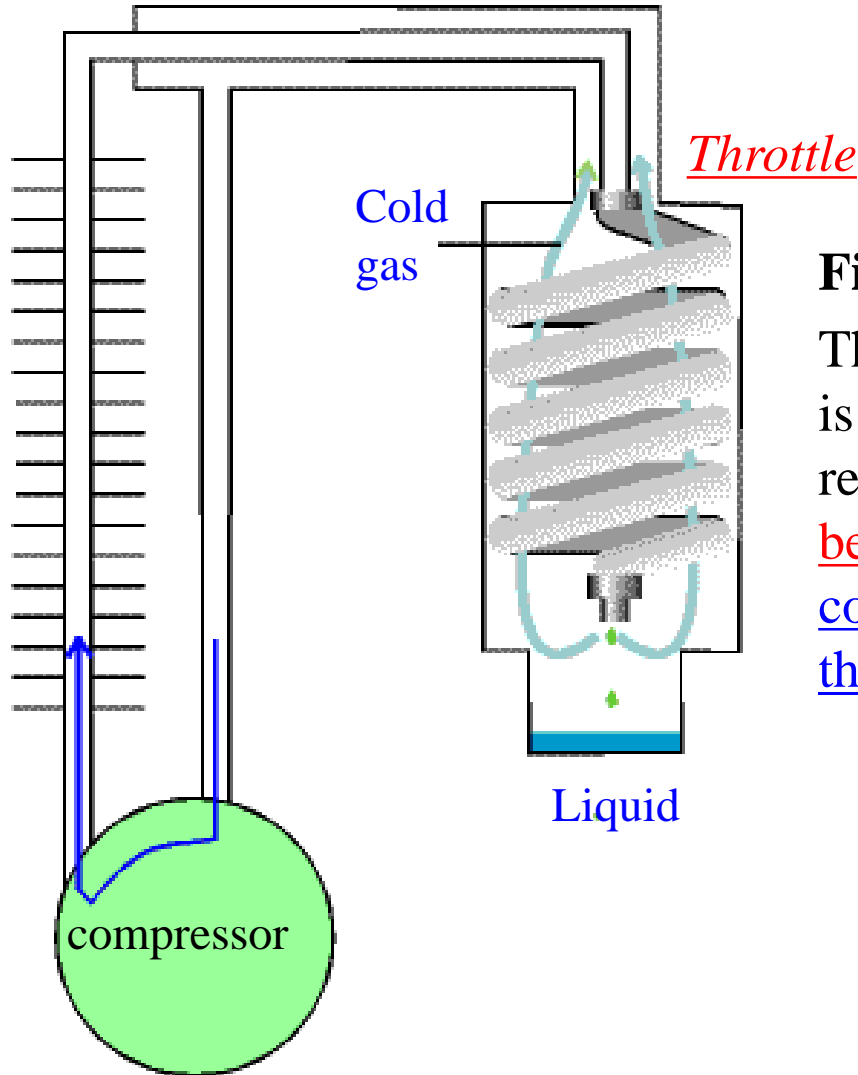


Figure 2D.12

The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated and, so long as it is beneath its inversion temperature, it cools on expansion through the throttle.

- Refrigerator
- Air Conditioner
- Vacuum Pump
- etc.

The Exact Relation between C_p and C_V

$$C_p - C_V = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V$$

$$H = U + pV$$

$$C_p - C_V = \left(\frac{\partial U}{\partial T} \right)_p + \left(\frac{\partial pV}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V$$

$$= C_V + \alpha V \left(\frac{\partial U}{\partial V} \right)_T + p \left(\frac{\partial V}{\partial T} \right)_p = p \alpha V$$

$$\begin{aligned} \therefore C_p - C_V &= \alpha V \left(\frac{\partial U}{\partial V} \right)_T + p \alpha V \\ &= \alpha V \left\{ p + \left(\frac{\partial U}{\partial V} \right)_T \right\} \end{aligned}$$

Definition of 'internal pressure'

$$\left(\frac{\partial U}{\partial V} \right)_T = \Pi_T$$

thermal-expansion coefficient

$$\alpha = \left(\frac{1}{V} \right) \left(\frac{\partial V}{\partial T} \right)_p$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad \text{(Derivation in Chap. 3)} \quad \text{ppt 2-58}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa} \quad \text{ppt 2-61 \& 2-62}$$

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p$$

thermal-expansion coefficient

$$\therefore C_p - C_V = \alpha V \left\{ p + \left(\frac{\partial U}{\partial V}\right)_T \right\} \quad \text{ppt 2-23}$$

$$= \alpha V \left\{ p + T\left(\frac{\partial p}{\partial T}\right)_V - p \right\}$$

$$= \alpha VT\left(\frac{\partial p}{\partial T}\right)_V = \alpha VT\left(\frac{\alpha}{\kappa}\right)$$

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

compressibility

$$C_p - C_V = \left(\frac{\alpha^2}{\kappa}\right) T V$$

General

For an ideal gas, $pV = nRT$.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \frac{nR}{p} = \frac{nR}{nRT} = \frac{1}{T} \quad \text{thermal-expansion coefficient}$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \frac{(-nRT)}{p^2} = \frac{nRT}{nRTp} = \frac{1}{p} \quad \text{compressibility}$$

$$\therefore C_p - C_V = \left(\frac{\alpha^2}{\kappa} \right) TV = \frac{1}{\frac{1}{p}} TV = \frac{p}{T^2} TV = \frac{nRT}{T} = nR$$

Problems

Chap. 2. The First Law of Thermodynamics

2A.2(b) 2A.3(b) 2A.4(b) 2A.4

2B.2 2B.3(b) 2B.4

2C.1(b) 2C.3(b) 2C.7(b)

2D.3(b) 2D.4(b) 2D.4

2E.2(b) 2E.3(b)