

CHEMISTRY(CY11001)

Professor: **Dr. Amita (Pathak) Mahanty**
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Ground Rules for the Class

- Mobile Phones in switched off mode
- Attendance is a must and will be checked regularly
- You are advised to take class notes

:Class Schedule (SECTIONS 1 & 2):

Room No.	Day	Time	
F-116	Monday	12:00 – 11:55 AM	Full Semester
	Tuesday	10:00 – 11:55 AM	Full Semester
	Thursday	02:00 – 2:55 PM (Sp Class)	upto 23.08.2019

LECTURE SCHEDULE FOR SECTIONS 1 & 2

CHEMISTRY THEORY

Topics	From	To	Classes
Phy. Chem. <u>Prof. APM</u>	29. 07. 2019 (Mon)	20. 08. 2019 (Tues)	13
Inorganic: <u>Prof. D. Ray</u>	22. 08. 2019 (Thurs)	14. 10. 2019 (Mon)	12
Organic: <u>Prof. NDPS</u>	15. 10. 2019 (Tues)	11. 11. 2019 (Mon)	12

IMPORTANT DATES:

PHY. CHEM. CLASS TEST	28. 08. 2019 (Wed) ; 6.00 – 6.30 PM; Venue: CIC (Tentative)	
MID SEMESTER EXAM	16. 09. 2019 (Mon) to	24. 09. 2019 (Tues)
END SEMESTER EXAM	18. 11. 2019 (Mon) to	27. 11. 2019 (Wed)

TUTORIAL SCHEDULE FOR CHEMISTRY (CY11001)

AUTUMN 2018-19

Sections 1 and 2

Section	Day	Time	Room No.	Roll No.
S-1-A	Tues	4.00 – 4.55 PM	F131	AE, AG, BT, CE, CH, CS, CY, EC, EE + Backlogs
S-1-B	Tues	4.00 – 4.55 PM	F132	EX, GG, HS, IE, IM, MA, ME, MI, MT, NA, PH, QD
S-2-A	Tues	4.00 – 4.55 PM	F233	AE, AG, BT, CE + Backlogs
S-2-B	Tues	4.00 – 4.55 PM	F234	CH, CS, CY, EC, EE

Dates of Physical Chemistry Tutorials

July 30

Aug 6

Aug 13

Aug 20

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Courses

► Autumn Semester - 2019

► Autumn Semester - 2018

► Agriculture & Food Engineering

Search courses:

GO

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Navigation

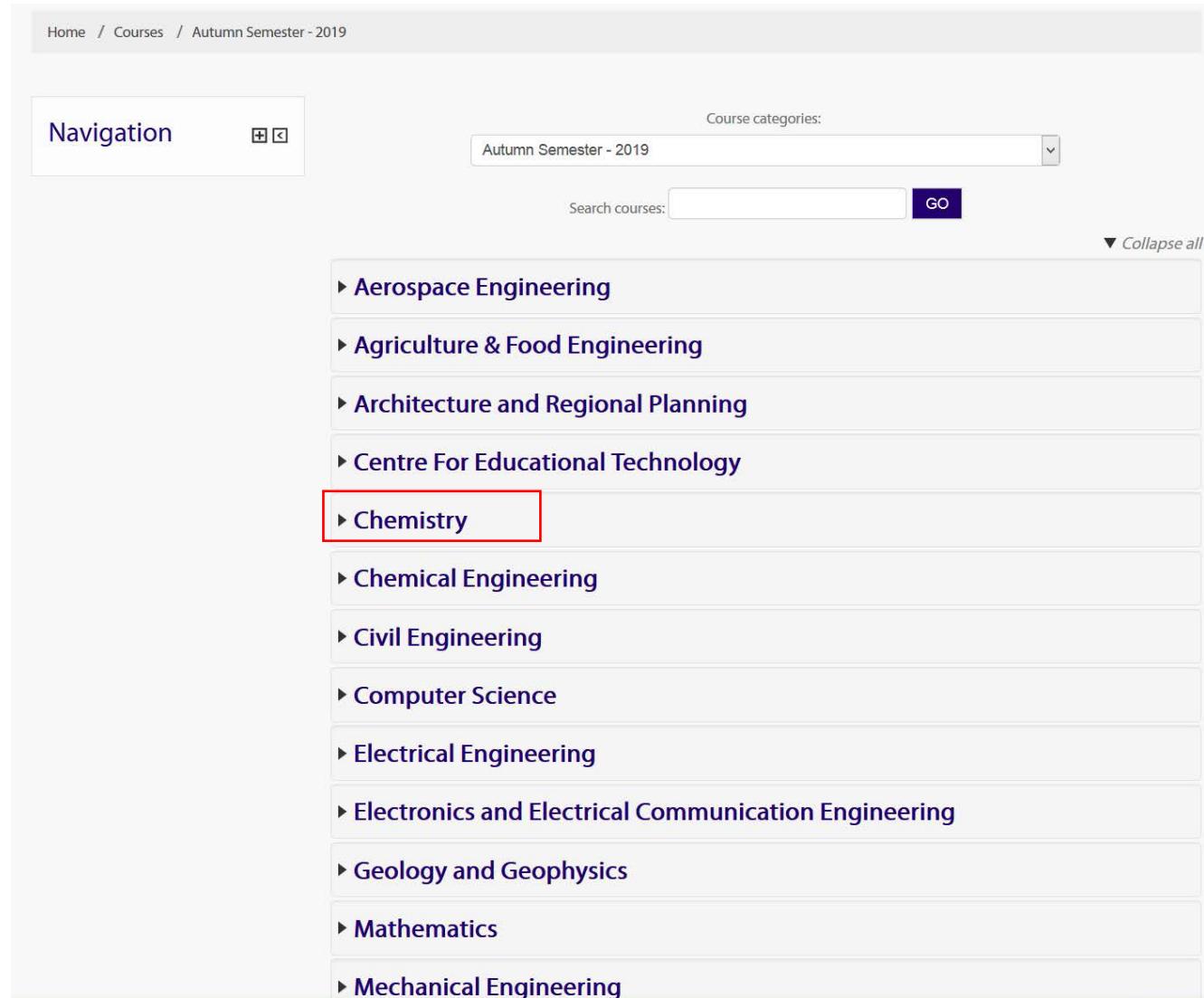
JULY 2019

Sun	Mon	Tue	Wed	Thu	Fri	Sat
1	2	3	4	5	6	
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31			

Online Users

(last 20 minutes)

<http://10.57.2.100/moodle/login/index.php>



The screenshot shows a Moodle course list interface. At the top, there's a navigation bar with 'Home / Courses / Autumn Semester - 2019'. Below it, a 'Navigation' box contains a 'Course categories:' dropdown set to 'Autumn Semester - 2019'. To the right is a search bar with 'Search courses:' and a 'GO' button. A 'Collapse all' link is also present. The main content area lists various courses under 'Course categories': Aerospace Engineering, Agriculture & Food Engineering, Architecture and Regional Planning, Centre For Educational Technology, Chemistry (which is highlighted with a red border), Chemical Engineering, Civil Engineering, Computer Science, Electrical Engineering, Electronics and Electrical Communication Engineering, Geology and Geophysics, Mathematics, and Mechanical Engineering.

Home / Courses / Autumn Semester - 2019

Navigation

Course categories:

Autumn Semester - 2019

Search courses: GO

▼ Collapse all

- ▶ Aerospace Engineering
- ▶ Agriculture & Food Engineering
- ▶ Architecture and Regional Planning
- ▶ Centre For Educational Technology
- ▶ Chemistry
- ▶ Chemical Engineering
- ▶ Civil Engineering
- ▶ Computer Science
- ▶ Electrical Engineering
- ▶ Electronics and Electrical Communication Engineering
- ▶ Geology and Geophysics
- ▶ Mathematics
- ▶ Mechanical Engineering

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CY 11001 CHEMISTRY

Distribution of Marks:

Mid Semester Exam (Only Physical): **30%**

End Semester Exam (Inorganic & Organic): **50%**

Teachers Assessment (TA): **20%**

TA Break up: [Physical **(6%)**, Inorganic **(7%)**, Organic **(7%)**]

TA marks to be based on ATTENDANCE / CLASS TEST

Text Book:

Atkin's Physical Chemistry 8th Ed

Reference Books:

Physical Chemistry by Silbey, Alberty & Bawendy; Wiley.

Physical Chemistry by I. N. Levine; McGraw.

Physical Chemistry by Gilbert W. Castellan; Narosa

CHEMISTRY (CY11001) (L-T-P : 3-1-0; Credit : 4)

Thermodynamics of Chemical Processes:

- Review of Essential Concepts and Definitions
- Revision: Heat, Work & Energy; First Law of Thermodynamics
- The Second Law of Thermodynamics
- Concept of Entropy
- Gibbs Free Energy
- Equilibrium conditions for Closed Systems
- Maxwell Relations
- The Chemical Potential
- Definition and Concept of Open Systems
- Phase and Reaction Equilibria

Electrochemical Systems:

- Electrochemical Cells and EMF
- Applications of EMF Measurements: Thermodynamic data, Activity Coefficients, Solubility product and pH

Thermodynamic

Primary Goal of Thermodynamics

- Determination of the equilibrium state that eventually results when the system undergoes a change in state
- Quantitative study of energy transformations associated with physical or chemical processes
- Thermodynamics provides a framework of relating the *macroscopic* properties of a system to one another based on few fundamental laws
- How and to what extent we can harvest energy from different sources

Thermodynamic

Thermodynamic: \leftrightarrow Classical, Statistical and Irreversible

Classical Thermodynamics is the study of **macroscopic properties** of system/matter **at equilibrium** (which **does not change with time**) using the laws governing transformation of energy from one form to another.

It is concerned **only** with macroscopic quantities and **ignores** the microscopic variables that characterize individual molecules.

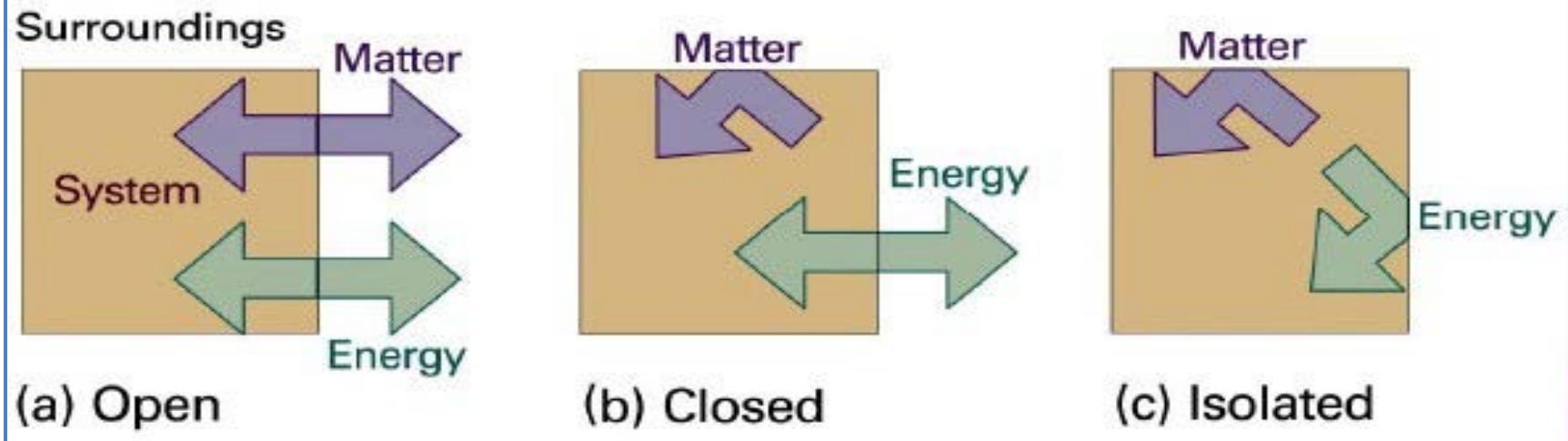
THE BASIC CONCEPTS:

- ❖ **System:** Part of the Universe, the properties of which is of interest.
- ❖ **Surroundings:** the region outside the system where we make our measurements.
- ❖ **Boundary,** a hypothetical/real barrier between system and surroundings.

System + Surroundings \rightarrow Universe

Thermodynamic

System and its Interaction with the Surroundings



System	Wall		Equilibrium State	
Open	Diathermal	Rigid	Permeable	T, V, μ
Closed	Diathermal	Rigid	Impermeable	T, V, N
	Diathermal	Flexible	Impermeable	T, p, N
Isolated	Adiabatic	Rigid	Impermeable	U, V, N

Thermodynamic Equilibrium

Equilibrium thermodynamics deals with systems in **Equilibrium**

Isolated system is in Equilibrium when its :

- a) Macroscopic properties do not change with time

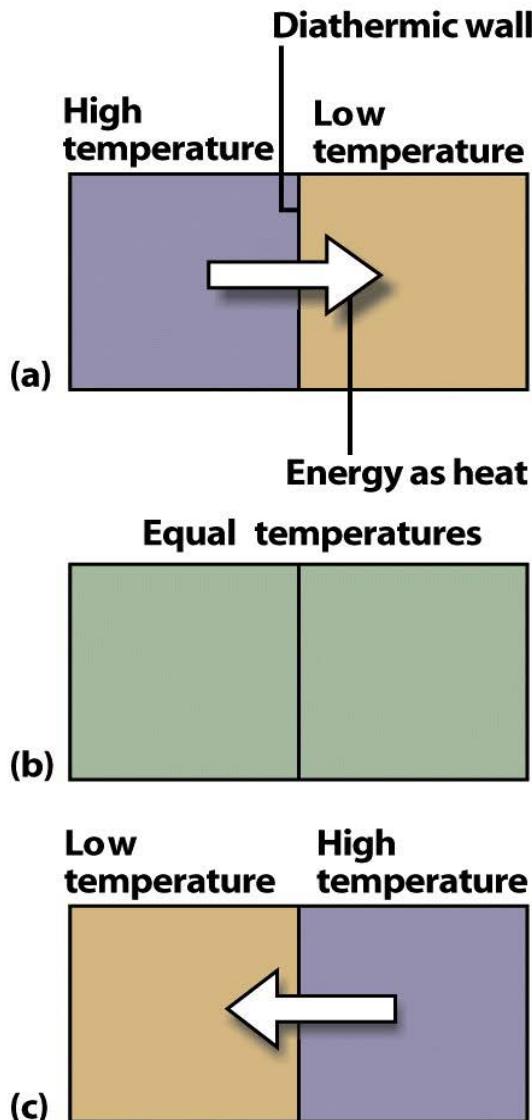
Non Isolated system is in Equilibrium when its:

- a) Macroscopic properties do not change with time
 - b) Removal of the system from contact with its surroundings can causes no change in the properties of the system
- A system in thermodynamic equilibrium is an **Equilibrium System**
 - **Thermodynamic State** only defined by the present values of the state variables, not by the history.

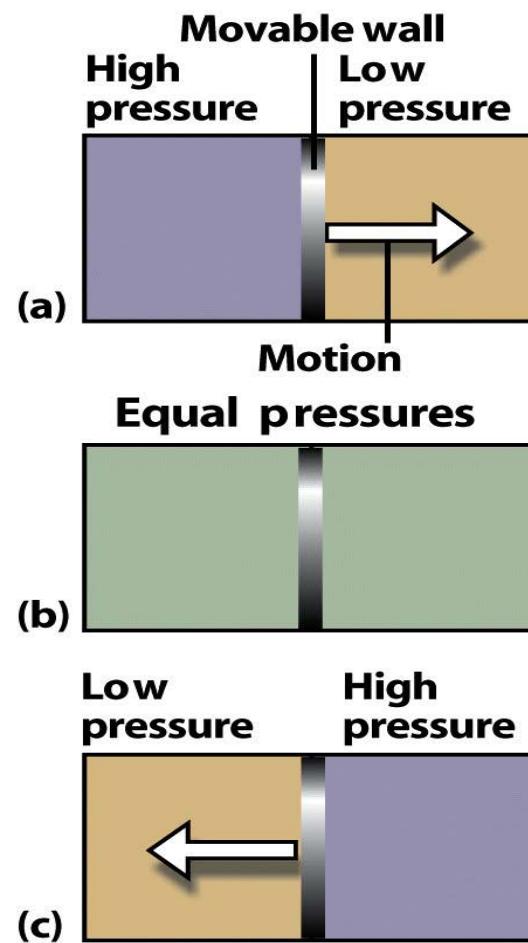
What are conditions of Thermodynamic Equilibrium?

Thermodynamic Equilibrium

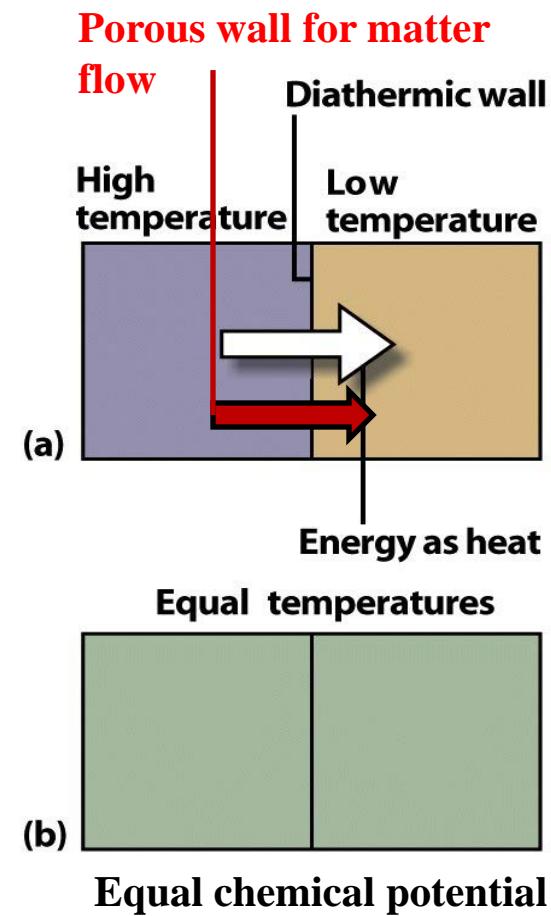
Thermal Equilibrium



Mechanical Equilibrium



Material Equilibrium



For thermodynamic equilibrium, all three kinds of equilibrium must be present

Thermodynamic Equilibrium

Thermal Equilibrium

between system and the surroundings, is a condition in which there is no change in the properties of the system or surroundings when they are separated by a **thermally conducting wall** **or**, a condition in which **no change of state occurs** when two objects A to B are in **contact through a diathermic boundary**

Mechanical Equilibrium

- There is **no change in the properties of the system or surroundings** when they are separated by a **movable wall / boundary**
- A condition of **equality of pressure** on either side of a **movable wall**.
- **No unbalanced forces act** on or within the system – system does not undergo acceleration or no turbulence inside the system

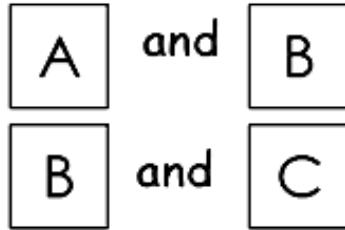
Material Equilibrium

A condition of **equality in concentrations** of the chemical species in the various parts of the system are **with time**. There is **no net transfer of matter from one part (phase) of the system to another or between the system and its surroundings**

An Important Macroscopic Parameter: **Temperature**

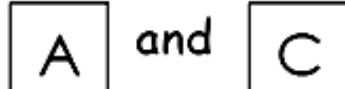
Temperature is a property associated with **random motion of many particles**. Introduction of the concept of **temperature** in thermodynamics is based on **the 0'th law of thermodynamics**:

If **A** and **B** are in thermal equilibrium and



are in thermal equilibrium,

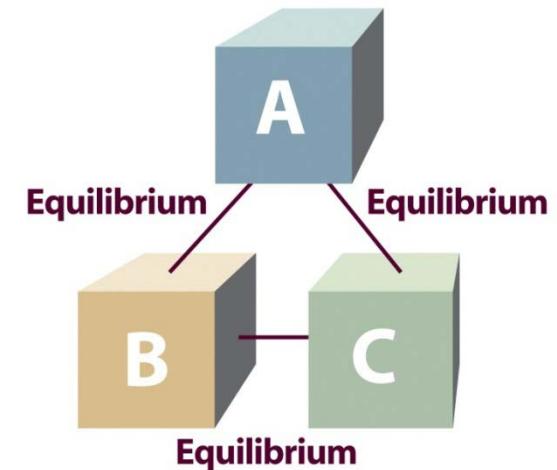
then **A** and **C** are in thermal equilibrium.



Consequence of the zero'th law:

B acts as Thermometer.

A, B, C all are at the same "temperature".



A well-defined quantity called **Temperature** exists such that **two systems** will be in **thermal equilibrium** if and only if both have the same temperature.

How to define a **Thermodynamic State** of System

What properties does thermodynamics use to characterize a system in equilibrium?

Macroscopic State of a System can be completely defined by a set of small number of macroscopic properties/parameters/physical characteristics or attributes of the system - **Thermodynamic Variables**

Thermodynamic variables which are experimentally measurable

- Composition – mass of each chemical species that is present in each phases,
- Pressure (P), Volume (V), Temperature (T), Density (ρ) etc.
- Field strength, if magnetic/electrical field act on the system

(N.B.: only the average values are considered, all fluctuation and perturbations are ignored).

On the other hand, **Microscopic State of a System** needs description of each molecule – a very complicated picture

Thermodynamic Variables

Intensive Properties

- Does not depend upon size (the quantity/amount of matter present) of the system [e.g. Pressure, Temp, Viscosity, Density etc.]

Total Property = property of part of the system

Extensive Properties

- Depends upon size of the system [e.g. n, V, surface area etc]
Extensive properties depend on the amount of substance in the system.]

Total Property = Σ property (in each part of the system)

Other variables:

Compositions, Surface area, Electrical/magnetic strength

Gravitational field can/are **generally ignored**

- **Homogeneous system**, a system having its **intensive macroscopic properties uniform throughout** → a single phase solution / pure substance.

- **Heterogeneous system**, a system with more than one phase.

Thermodynamic State Variables / Properties

The **change** in a **STATE VARIABLE** depends only on the **INITIAL** and **FINAL** state of the thermodynamic property, and is **INDEPENDENT** of the **PATH** taken during execution of the process

HOW MANY STATE VARIABLES WILL BE REQUIRED TO DESCRIBE A MACROSCOPIC STATE??

- ONLY **3** of these **4** variables (**T, P, V** and **the amount of species**) are needed to be specified to describe a System. Of these, ONLY **3** variables need to be specified; while the **4th** variables can be calculated from the **Equation of State**
- A Thermodynamic State of a specified amount of **PURE SUBSTANCE** (i.e., no of species = 1) in fluid state can be described by specifying ONLY **2** of these **3** variables (**T, P, V**), when the amount of the substance is fixed - (i.e., **T and P; P and V** or, **T and V**). All other thermodynamic variables are fixed and the system is in Equilibrium.

Therefore, more variable have to be specified to describe the Thermodynamic State of a homogeneous mixture of different species

Thermodynamic State Variables / Properties

Intensive State: A Thermodynamic State **described by Intensive Variables**

Intensive State of PURE Substance in fluid state can be described by specifying **($N_s + 1$) variables** where, N_s is the number of different kind of species present in a system

Extensive State: A Thermodynamic State described by **Intensive Variables plus at least ONE Extensive variable**

Extensive State of PURE Substance in fluid state can be described by specifying **($N_s + 2$) variables** where, **ONE** of the variable must be **Extensive** (N_s is the number of different kind of species present in a system)

Therefore, for describing the State of a System we require:

- A few experimentally measureable macroscopic properties: p, T, V, n, m, ...
- Knowledge if System is Homogeneous or Heterogeneous
- Knowledge if System is in Equilibrium State
- Knowledge of the number of components

Thermodynamic State

- If the value of every thermodynamic property in system A is same as in system B – **then they are in the same thermodynamic state**
- The **state of a thermodynamic system** is defined by specifying the values of its thermodynamic properties – However, it is not necessary to specify all the properties to define the state of a system.
- In fact, **the macroscopic state** of a system can be completely defined by a small set **of macroscopic variables** – these are **called** the **Thermodynamic Properties / Parameters / Variables of a system**.

For instance: The thermodynamic state of a **single-phase system of fixed amounts** of non reacting substances can be described by any two of the three state functions (P, V and T)

Equation of State, an equation that interrelates pressure, volume, temperature, and amount of substance: $P = f(T, V, n)$.

The Equation of State of Ideal Gases

- An equation of state - an equation that relates macroscopic variables (e.g., P , V , and T) of a given substance in **thermodynamic equilibrium**.
- In equilibrium (\equiv No macroscopic motion), just a *few macroscopic* parameters are required to describe **the state of a system**.
- Geometrical representation of the **equation of state**: $f(P,V,T) = 0$

The Ideal Gas Equation of State: $PV = nRT$

P – pressure

[**Newton/m²**]

V – volume

[**m³**]

n – number of moles of gas

T – the temperature in Kelvins [**K**]

R – a universal constant = **8.314 J mol⁻¹K⁻¹**

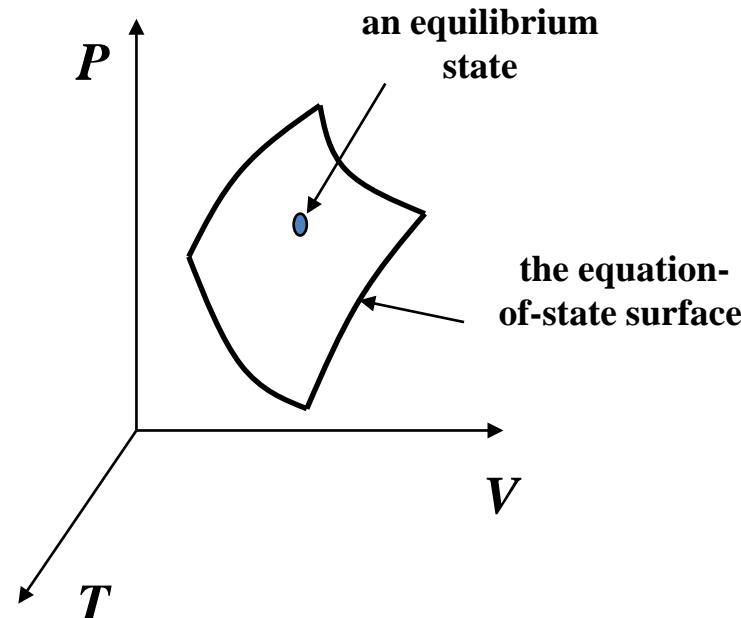
$8.205\ 74 \times 10^{-2}$ dm³ atm K⁻¹ mol⁻¹

$8.314\ 47 \times 10^{-2}$ dm³ bar K⁻¹ mol⁻¹

$8.314\ 47$ Pa m³ K⁻¹ mol⁻¹

$1\ 62.364$ dm³ Torr K⁻¹ mol⁻¹

$1.987\ 21$ cal K⁻¹ mol⁻¹



The Equation of State of Ideal Gases

This is a mathematical relationship between appropriate thermodynamic variables of a system at equilibrium

e.g. $f(p, V, T) = 0$

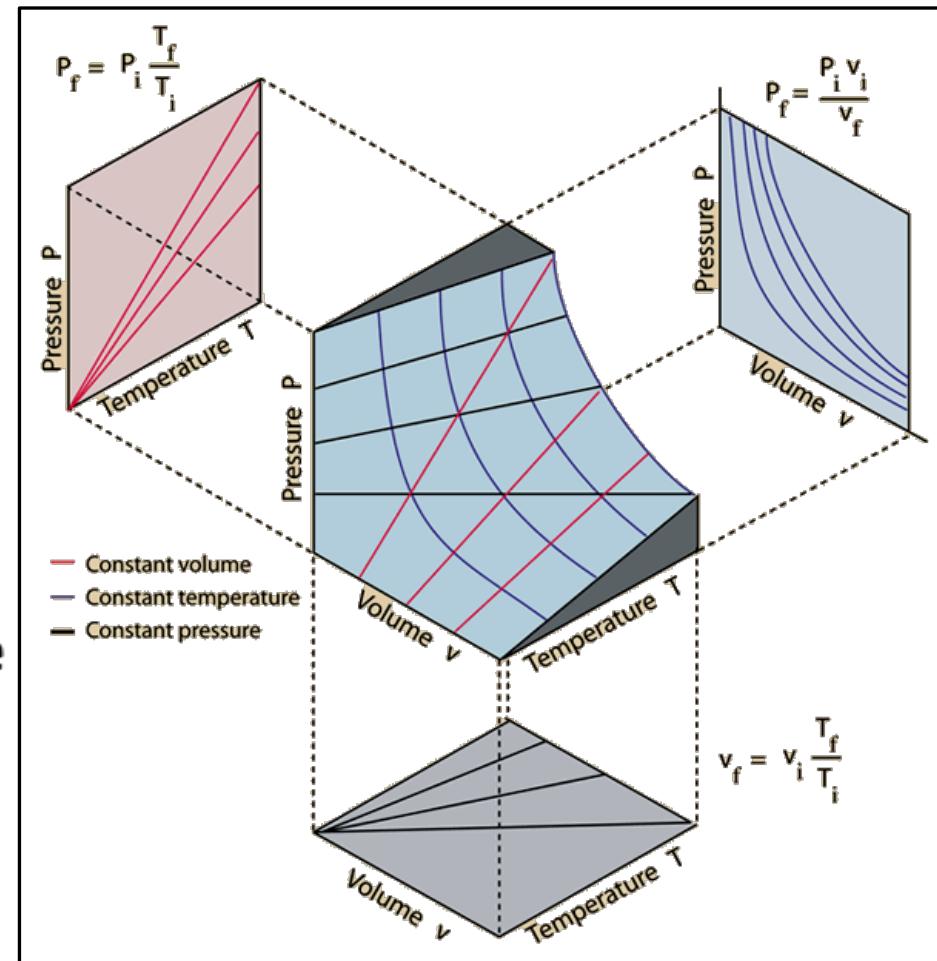
Example

- Ideal gas equation of state

$$pV = nRT$$

- van der Waals equation of state

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$



The Gas Laws and Definitions (Recap)

- **Boyle's law:** At constant temperature, the pressure of a sample of gas is inversely proportional to its volume, $p \propto 1/V$ at constant temperature.
- **Charles' law:** At constant pressure, the volume of a gas is proportional to the absolute temperature $V \propto T$ at constant pressure.
- **Avogadro's principle:** Equal volumes of gases at the same pressure and temperature contain the same numbers of molecules
- **Partial pressure**, of a gas is the pressure the gas would exert if it occupied the container alone; in general, $p_i = x_i P$
- **Vapour pressure**, the pressure of a vapour in equilibrium with its condensed phase
- **Mole fraction**, the amount of i species, expressed as a fraction of moles of the moles of i th species (n_i) to the total amount of moles, n , in the sample,
 $x_i = n_i/n$

Appendix

- **Perfect / Ideal gas equation, $pV = nRT$**
- **Perfect/ideal gas**, a gas that obeys $pV = nRT$ exactly under all conditions.
- **Real gas**, an actual gas. e.g., $\left[P + a\left(\frac{n}{V}\right)^2 \right] \left(\frac{V}{n} - b \right) = RT$
- **Standard ambient temperature and pressure (SATP)**, 298.15 K (25 °C) and 1 bar (or, 0.986 atm or 100 kPa).
- **Standard temperature and pressure (STP)**
273.15 K (0 °C) and 1 bar (100 kPa, 0.986 atm.)
- **Normal temperature and pressure (NTP)**
273.15 K (0 °C) and 1 atm (101.325 kPa, 760 Torr)
- **gas constant, R** (with $R = N_A k$, where N_A is Avogadro's constant and k is Boltzmann's constant).

1 atm = (101.325 kN/m², 101.325 kPa, 14.7 psi, 29.92 in Hg, 760 torr).

Appendix

Table A1.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	$1 \text{ kg m}^{-1} \text{s}^{-2}$ 1 N m^{-2}	pascal, Pa
Energy	$1 \text{ kg m}^2 \text{s}^{-2}$ 1 N m 1 Pa m^3	joule, J

Table A1.4 Some common units

Physical quantity	Name of unit	Symbol for unit	Value*
Time	minute	min	60 s
	hour	h	3600 s
	day	d	86 400 s
Length	ångström	Å	10^{-10} m

Thermodynamic Process: Operation for Change in State

Change of State: Transformation

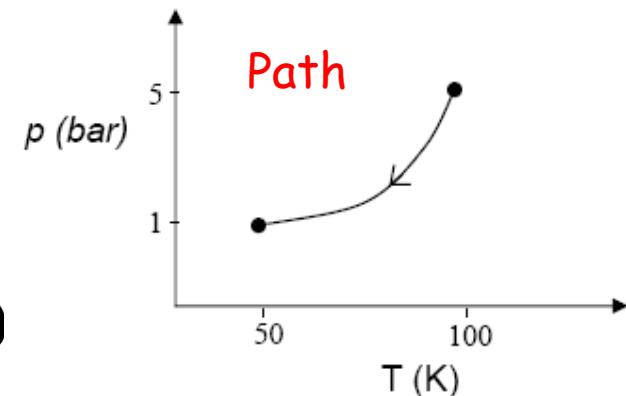


Path: Sequence of Intermediate states, arranged in order, through which a system passes to attain the final state

Process: Operation through which a system undergoes a change in state.
Process describes the path.

Path can be:

- ✓ Reversible (always in Equilibrium)
- ✓ Irreversible (describes direction of time)
- ✓ Cyclic (initial and final state have the same value)

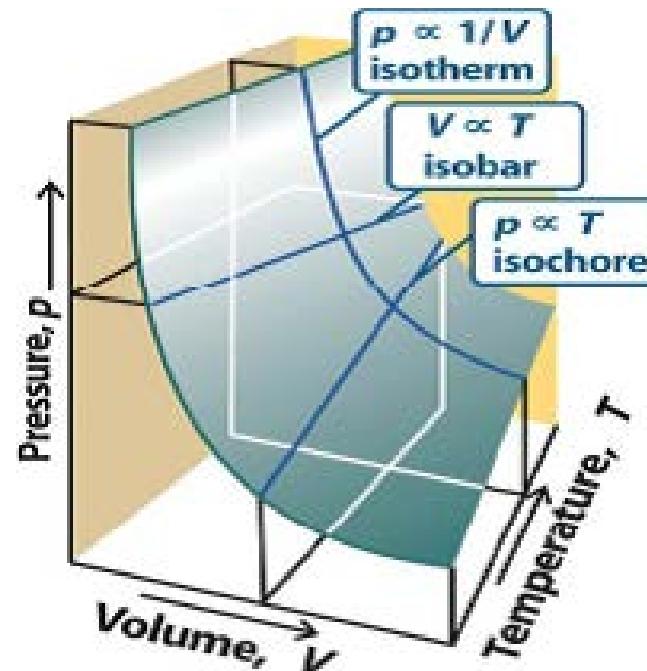
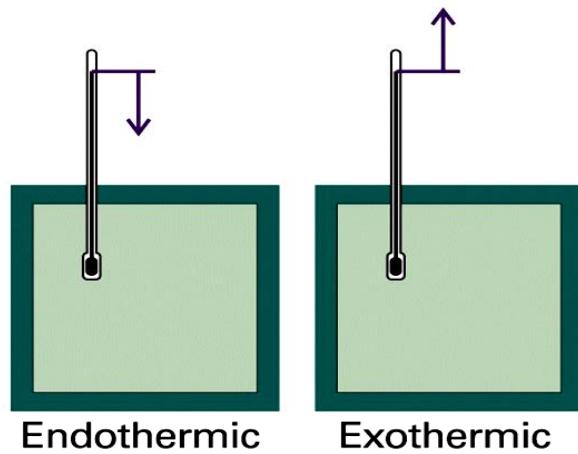


Processes can be:

- Adiabatic (No heat transfer between system and surrounding)
- Isobaric (Constant pressure process)
- Isothermal (Constant temp process)
- Constant Volume process
- Endothermic & Exothermic process ($q < 0$ & $q > 0$)

Thermodynamic Process: Operation for Change in State

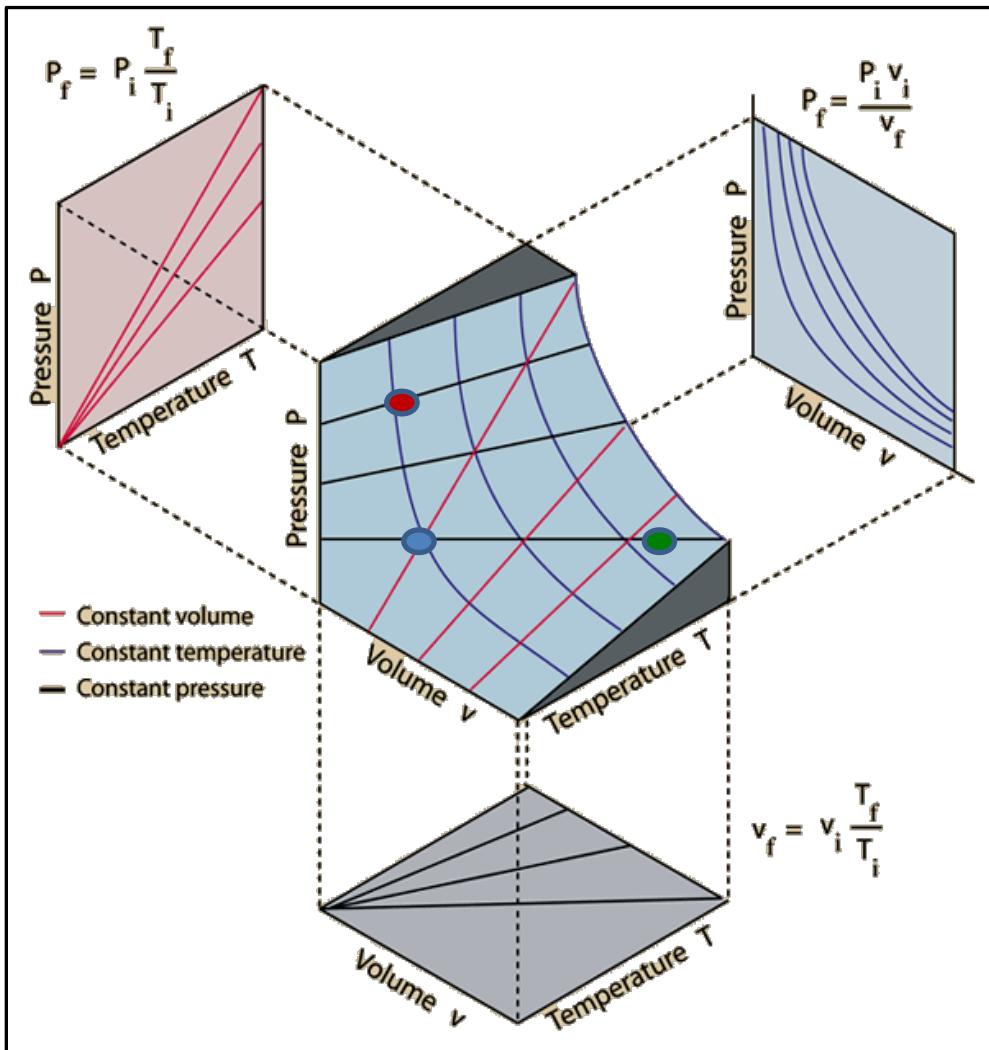
Processes : When one or more of the parameters of a system changes, the **state** of the system also **changes** and the system is said to have undergone a process.



Each process can be either carried out either
REVERSIBLY or **IRREVERSIBLY**

Thermodynamic Processes in a Closed System

From an initial equilibrium state to a final equilibrium state



Various types of Processes:

- Isothermal (constant T),
- Isobaric (constant p),
- Isochoric (constant V)
- Adiabatic (no heat transfer)
- Isenthalpic (constant enthalpy, H)
- Exothermic & Endothermic
- Cyclic

Each of these process can be either carried out **Reversibly** or **Irreversibly**

Thermodynamic Processes can be :

Reversible process: Ideal process

- Change must occur in successive stages of infinitesimal quantities
- Infinite duration
- Virtual thermodynamic equilibrium, at each of the small stages.
- Changes of the thermodynamic quantities in the different stages will be the same as in the forward direction but opposite in sign w.r.t. forward direction. The system and surroundings can be put back in their original states by exactly reversing the process.

Irreversible Process: Real / Spontaneous

- Occurs suddenly or spontaneously without the restriction of occurring in successive stages of infinitesimal quantities. Irreversible processes cannot be undone by exactly reversing the change to the system.
- Do not remain in the virtual equilibrium during the transition.
- The work (w) in the forward and backward processes would be unequal.

Cyclic process: • Is one in which the initial and final states are the same.

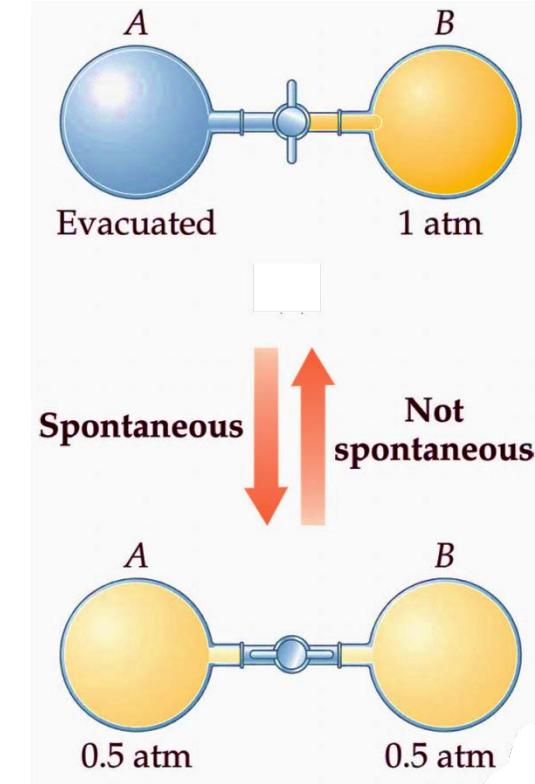
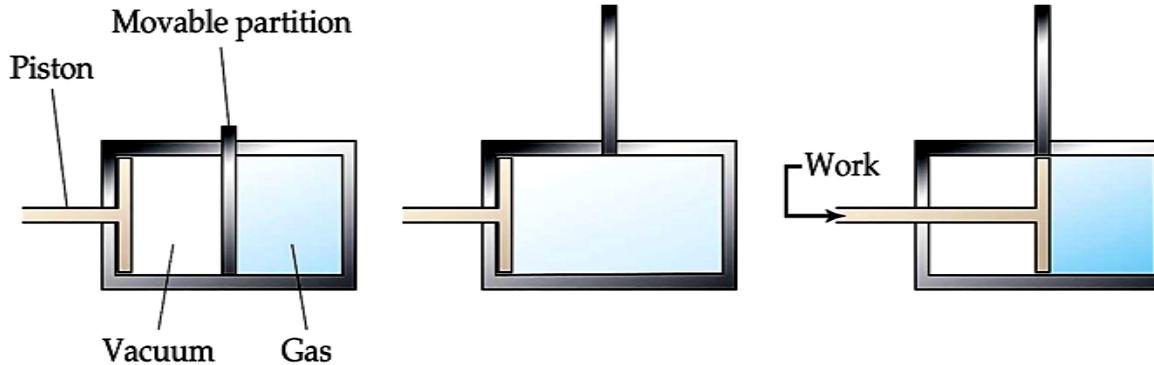
In such process:

- There is no change in the STATE VARIABLES (e.g., $\int dU = U_f - U_i = 0$)
- In contrast, path functions generally have non-zero values for cyclic processes, dependent on the path (e.g., $\int \delta w \neq (w_f - w_i) \neq 0$). PATH VARIABLE

Thermodynamic Processes: Irreversible Process

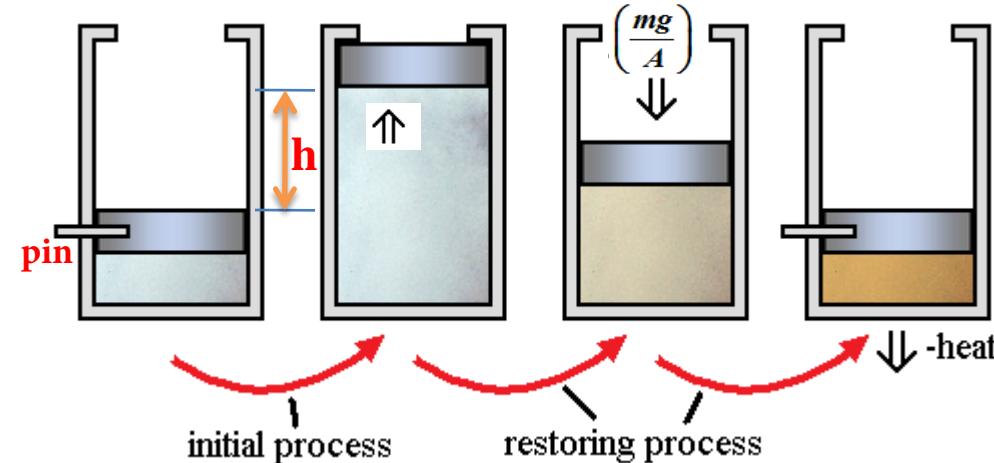
Spontaneous Process (Irreversible Process)

- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it can *not* spontaneously go back to *B*



- Irreversible processes cannot be undone by exactly reversing the change to the system.
- All Spontaneous processes are irreversible.
- All Real processes are irreversible.

Thermodynamic Processes: Irreversible Process

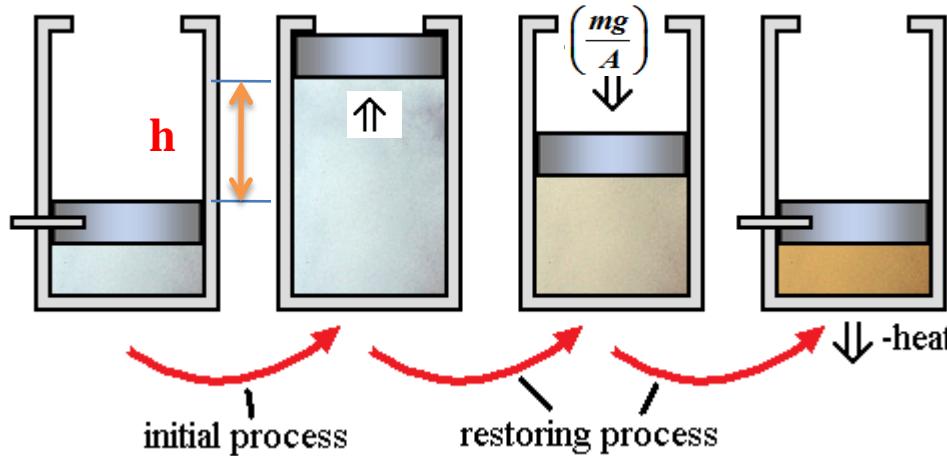


Consider a gas restrained at high pressure by a piston that is secured by a pin.

When the pin is removed, the piston is raised and forced abruptly against the stops

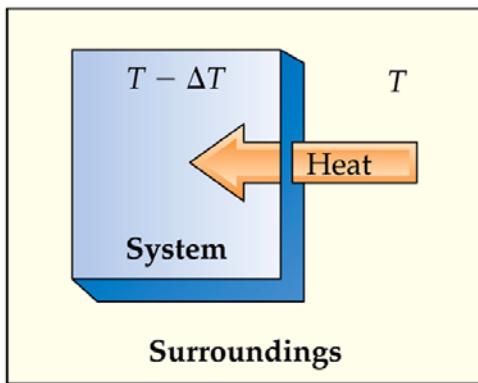
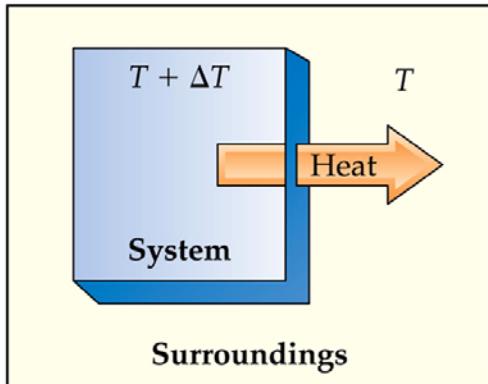
- **Work, (w_{exp})**, is done by the system, since the piston has been raised by h .
- To restore the system to its initial state, force has to be exerted on the piston to compress the gas
- Since the pressure on the face of the piston is greater on the restoring compression process than on the initial expansion process. Therefore the work done on the gas in this restoring compression process is greater, (w_{comp}), than the work done by the gas in the initial expansion process (w_{exp}).
- Again, to restore the gas to its original internal energy, some amount of heat must be transferred from the gas during the restoring compression process.

Thermodynamic Processes: Irreversible Process

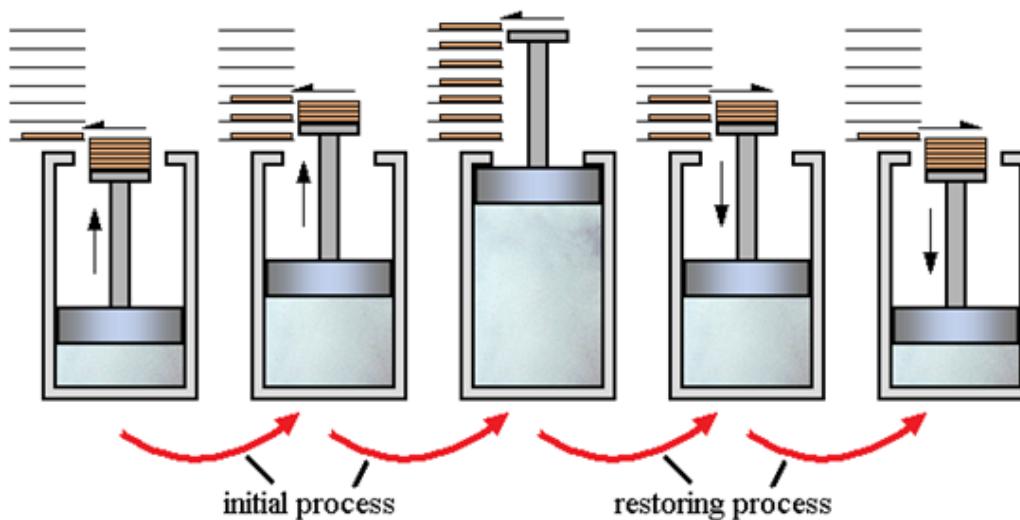


- Thus, the system can be restored to its initial state, but the surroundings have changed by virtue of the fact that work was required to force the piston down and heat was transferred to the surroundings.
- The initial process **therefore** is an IRREVERSIBLE one because it could NOT BE REVERSED TO ITS ORIGINAL STATE WITHOUT LEAVING A CHANGE IN THE SURROUNDINGS.

Thermodynamic Processes: Reversible Process



- In a **reversible process** the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.
- Changes are **infinitesimally small** in a reversible process.
- Quasi thermodynamic equilibrium, at each of the small stages



Reversible and Irreversible Processes

Reversible processes

- Occur in **infinite number of steps** and **slowly** pass through successive stages of **infinitesimal quantities**
- Virtual thermodynamic equilibrium at each of the small stages
- Backward changes of the thermodynamic quantities at every stage is the **same as in the forward direction** but opposite in sign

Irreversible processes

- Occur rapidly in a **single step**
- Do not remain in thermodynamic equilibrium while passing from initial to final state
- Forward and backward changes of the thermodynamic quantities are **unequal**
- Can not be reversed to its original state **WITHOUT** leaving a change in the surroundings

Understanding the Change in State

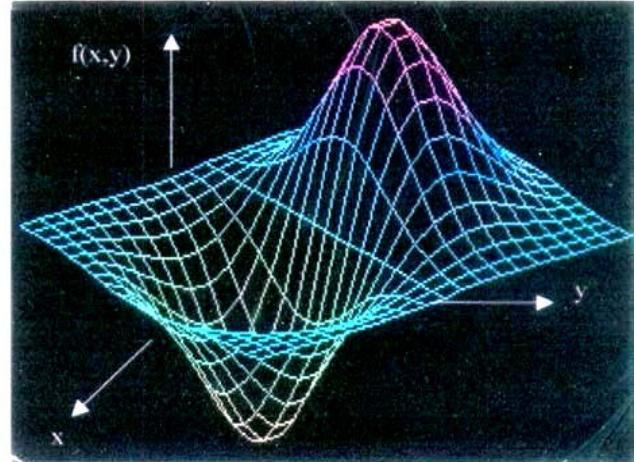
**Mathematical Foundation
of
Thermodynamics**

Partial Differentiation: A Primer

- Consider a function of two variables

$$f(x, y)$$

- A partial derivative of f :
the rate of change of the function f
w.r.t. one variable with all other
variables kept fixed.



$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}$$

$$\left(\frac{\partial f}{\partial y}\right)_x = \lim_{\Delta y \rightarrow 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}$$

$$f(x, y) = x^2 y$$

$$\left(\frac{\partial f}{\partial x}\right)_y = 2xy$$

$$\left(\frac{\partial f}{\partial y}\right)_x = x^2$$

Properties of Partial Derivatives

- 1st order Differential of $f(x, y)$

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

- 2nd order partial derivative of $f(x, y)$

Let $\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) = \frac{\partial^2 f}{\partial x \partial y}$ $\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) = \frac{\partial^2 f}{\partial y \partial x}$

For $f(x, y) = x^2 y$, $\left(\frac{\partial f}{\partial x} \right)_y = 2xy$ and $\left(\frac{\partial f}{\partial y} \right)_x = x^2$

$$df = 2xy dx + x^2 dy$$

$$\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial x} (x^2) = \underline{2x} \quad \text{and} \quad \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) = \frac{\partial}{\partial y} (2xy) = \underline{2x}$$

Exact Differential.

The Exact Differential

General expression for the total differential of $f(x, y)$

$$df = M(x, y)dx + N(x, y)dy$$

where

$$M = \left(\frac{\partial f}{\partial x} \right)_y \quad \text{and} \quad N = \left(\frac{\partial f}{\partial y} \right)_x$$

Question:

Would any expression $M(x, y)dx + N(x, y)dy$ always represent the total differential of a function?

If and only if,

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

then, $df = M(x, y)dx + N(x, y)dy$ is an exact differential

Examples of Exact Differentials

- **Example 1** $2xy \, dx + x^2 \, dy$ $M = \left(\frac{\partial f}{\partial x}\right)_y \quad N = \left(\frac{\partial f}{\partial y}\right)_x$
 $df = M(x,y)dx + N(x,y)dy$
 $M = 2xy \quad N = x^2 \Rightarrow 2xy \, dx + x^2 \, dy = d(x^2y)$
Here, $f = (x^2y)$

- **Example 2** $3x^2y^2 \, dx + 2x^3y \, dy$
 $df = M(x,y)dx + N(x,y)dy$
 $M = 3x^2y^2 \quad N = 2x^3y \Rightarrow 3x^2y^2 \, dx + 2x^3y \, dy = d(x^3y^3)$
Here, $f = (x^3y^2)$

Integration of an Exact Differential

- Let us move from an initial point (x_i, y_i) to a final point (x_f, y_f)

- The associated change in $f(x, y)$ is

$$\Delta f = \mathbf{f}(x_f, y_f) - \mathbf{f}(x_i, y_i) = \int_{\mathbf{i}}^{\mathbf{f}} df = \int_{\mathbf{i}}^{\mathbf{f}} (Mdx + Ndy)$$

- The value of Δf

- depends on the values of $f(x, y)$ at the initial and final points only
- is independent of the path taken in going from the initial to the final state

- For a closed path, $\mathbf{i} = \mathbf{f}$ and $\oint df = 0$

Integral of an Exact Differential function, df , for a closed path (i.e., cyclic) where, i (initial state) = f (final state): is always $\oint df = 0$

Inexact Differential

The expression $df = M(x, y)dx + N(x, y)dy$ does not represent an exact differential if:

$$\left(\frac{\partial M}{\partial y} \right)_x \neq \left(\frac{\partial N}{\partial x} \right)_y$$

where, $M = \left(\frac{\partial f}{\partial x} \right)_y$ and $N = \left(\frac{\partial f}{\partial y} \right)_x$

Example:

- $M = y \quad N = 0 \quad dz = y dx$
- $M = 0 \quad N = x \quad dz = x dy$
- $M = y(xy + 1) \quad N = -x \quad dz = y(xy + 1) dx - x dy$

In all these cases, dz is an inexact differential

Useful Properties of Inexact Differentials

- The sum of two inexact differentials can be equal to an exact differential

Case 1: $\delta z' = y \, dx$ is an inexact differential

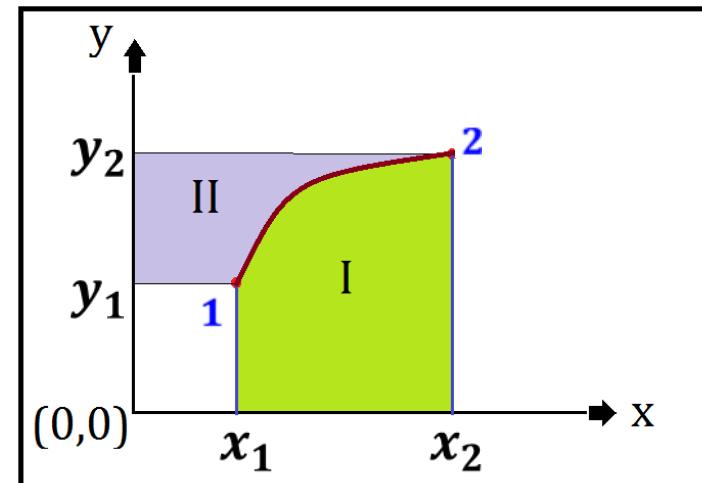
$$\int_1^2 \delta z' = \int_{x_1}^{x_2} y \, dx = \text{Area I}$$

where y varies along a chosen path

Case 2: $\delta z'' = x \, dy$ is an inexact differential

$$\int_1^2 \delta z'' = \int_{y_1}^{y_2} x \, dy = \text{Area II}$$

where x varies along the same chosen path

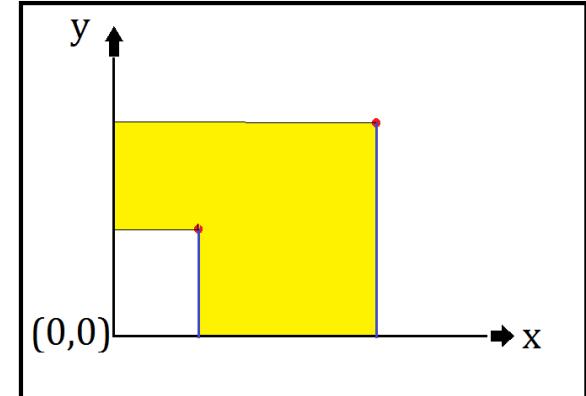
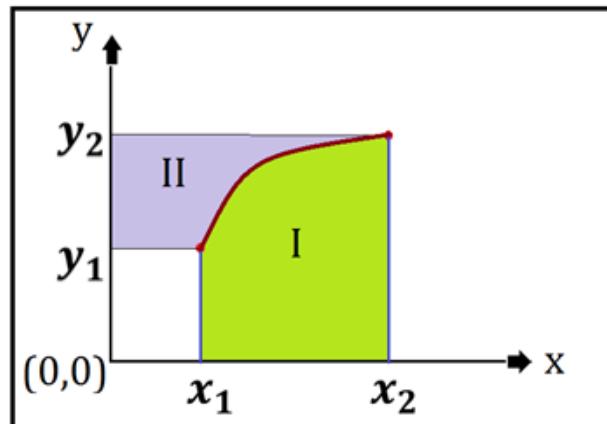


Useful Properties of Inexact Differentials

- The sum of two inexact differentials can be equal to an exact differential

Case 3: $dz = d(xy)$ is an exact differential

$$\int_1^2 dz = \int_1^2 d(xy) = x_2 y_2 - x_1 y_1$$



$$\int_1^2 dz = x_2 y_2 - x_1 y_1 = \int_1^2 \delta z' + \int_1^2 \delta z''$$

$$dz = \delta z' + \delta z''$$

Therefore, the sum of these areas is independent of the path between 1 and 2 therefore,
SUM of two path function results in a STATE function

Useful Properties of Inexact Differentials

- Multiplication of an **inexact differential** by an **integrating factor** can be equal to an **exact differential**

Example

Inexact differential

$$\delta z = y(xy + 1) dx - xdy$$

Integrating factor

$$\tau = \frac{1}{y^2}$$

Thus, $\frac{\delta z}{y^2} = \left(x + \frac{1}{y}\right) dx + \left(-\frac{x}{y^2}\right) dy = d\left(\frac{x(xy+2)}{2y}\right)$

Defining $f = \frac{x(xy+2)}{2y}$, we get

$$\tau \delta z = df$$

Useful Properties of Inexact Differentials

For example:

Let the differential form of the physical quantity will be :

$$df(x, y) = y(xy + 1)dx - xdy$$

$$\equiv df = [M(x,y) dx + N(x,y) dy]$$

$$\text{here, } M = \left(\frac{\partial f}{\partial x} \right)_y = y(xy + 1); \text{ and } N = \left(\frac{\partial f}{\partial y} \right)_x = x$$

$$\therefore \left(\frac{\partial M}{\partial y} \right)_x = \left| \frac{\partial [y(xy + 1)]}{\partial y} \right|_x = 2xy + 1$$

$$\text{and, } \left(\frac{\partial N}{\partial x} \right)_y = \left| \frac{\partial [-x]}{\partial x} \right|_y = -1$$

$$\text{So, } \left(\frac{\partial M}{\partial y} \right)_x \neq \left(\frac{\partial N}{\partial x} \right)_y$$

Therefore, it is an Inexact Differentials

Let the Integrating factor be: $\left(\frac{1}{y^2} \right)$

$$\text{So, } df' \equiv \frac{df}{y^2} = \left(x + \frac{1}{y} \right) dx - \frac{x}{y^2} dy$$

Obtaining Exact Differentials From Inexact Differentials

Multiplying by the Integrating factor $\left(\frac{1}{y^2}\right)$ we get:

$$df' \equiv \frac{df}{y^2} = \left(x + \frac{1}{y} \right) dx - \frac{x}{y^2} dy$$

Mixed partial derivatives

$$\left\{ \begin{array}{l} \left| \frac{\partial[(x + 1/y)]}{\partial y} \right|_x = -\frac{1}{y^2} \\ \left| \frac{\partial[(-x/y^2)]}{\partial x} \right|_y = -\frac{1}{y^2} \end{array} \right.$$

The function f' defined by : $f'(x, y) = \frac{x^2}{2} + \frac{x}{y}$

Integrating factors are useful for obtaining **exact differentials** from **inexact differentials** and in solving first-order differential equations.

Properties of Partial Derivatives

- **The Chain Rule**

Let s be an independent parameter such that change of s results in changes in the values of x and y

$x = x(s)$, $y = y(s)$ Thus, $f(x, y) \equiv f(s)$

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

- **The Cyclic Rule $f(x, y)$**

- For $z = z(x, y)$,

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

Test for Exactness (State Variable)

If $\mathbf{z} = f(x, y)$

Then, **Total Differential of z** is :

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

if, $M = \left(\frac{\partial z}{\partial x} \right)_y$; and $N = \left(\frac{\partial z}{\partial y} \right)_x$

Then, $dz = M dx + N dy$

And **Condition for Exact Different:**

$$\Rightarrow \left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

$$\Rightarrow \left[\frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x} \right)_y \right]_x = \left[\frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y} \right)_x \right]_y$$

$$\Rightarrow \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

dz will be a perfect differential when it is found →

- dz is a single-valued function depending entirely on the instantaneous values of x and y .
- dz between any two specified points or states is **independent of the path of transition**.
- dz for a complete cyclic process is **equal to zero**
- δq and δw are **NOT EXACT differential** quantities therefore they are **NOT STATE Variables. They are PATH FUNCTIONS.**

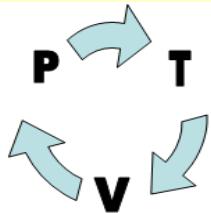
Properties of Partial Derivatives

- The Cyclic Rule:

Example:

If $V = f(p, T)$; $p = f(V, T)$; $T = f(p, V)$, then we can write

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



Example 1:

Use the Equation of state for Ideal gas to verify the cyclic rule

$$p = nRT/V; V = nRT/p; T = pV/nR$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} \quad ; \quad \left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{nR} \quad ; \quad \left(\frac{\partial V}{\partial p}\right)_T = \frac{-nRT}{p^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{nR}{V}\right) \left(\frac{p}{nR}\right) \left(\frac{-nRT}{p^2}\right) = -\left(\frac{nRT}{pV}\right) = -1$$

Application of Partial Derivatives

Function:

$$z = f(x, y) \rightarrow$$

Total differential forms:

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

$$V = f(p, T) \rightarrow dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$$

$$p = f(V, T) \rightarrow dp = \left(\frac{\partial p}{\partial T} \right)_V dT + \left(\frac{\partial p}{\partial V} \right)_T dV$$

$$T = f(p, V) \rightarrow dT = \left(\frac{\partial T}{\partial p} \right)_V dp + \left(\frac{\partial T}{\partial V} \right)_p dV$$

$$\frac{\partial^2 T}{\partial p \partial V} = \frac{\partial^2 T}{\partial V \partial p} = \frac{1}{R} \quad (\text{for Ideal Gas})$$

$$\alpha(T, p) = \frac{1}{T} \quad (\text{For Ideal Gas}); \quad \kappa_T(T, p) = \frac{1}{p} \quad (\text{For Ideal Gas})$$

- How fast the (fraction of) volume increases with temperature is given by: α (*the Isobaric Expansion coefficient*)

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

- How fast the (fraction of) volume decreases with pressure is given by: κ_T (*the Isothermal Compressibility*)

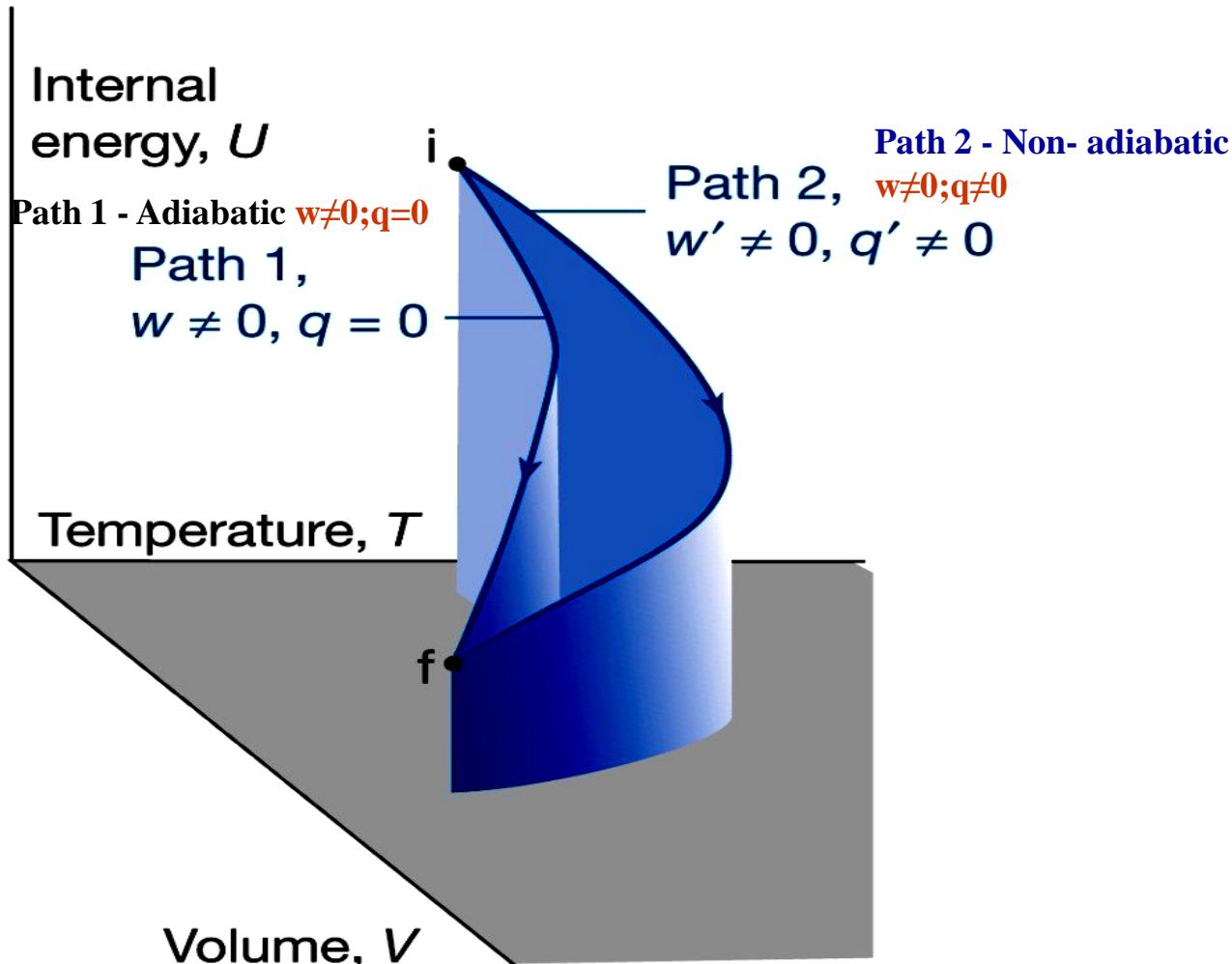
$$\kappa_T(T, p) = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

STATE AND PATH FUNCTIONS

- Some **state functions**, e.g., U and H etc.
 - Value of a state function is **independent of path**
 - Depends only on initial and final state, e.g. $\Delta U = U_{\text{final}} - U_{\text{initial}}$
 - **Overall Change:** $\Delta U = \int_{\text{initial}}^{\text{final}} dU \Rightarrow dU \text{ is an } \underline{\text{exact differential}}$
 - For ΔU , work may be done, or, heat may flow or, both
- Path from initial to final state has a functional dependence
 - Equations that describe how you get to final state are path functions
 - **Path functions are path specific**

$$\partial q = \int_{\text{initial}}^{\text{final}} \partial q \Rightarrow \partial q \text{ is an } \underline{\text{inexact differential}}$$

State and Path Functions



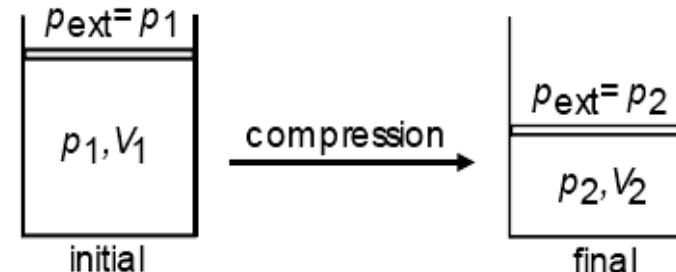
$$\Delta U_{\text{path1}} = \Delta U_{\text{path2}} = U_f - U_i$$

Is Work a STATE FUNCTION?

Assume a Reversible process so that $p_{ext} = p$ where, Ar (gas) under goes change of state through compression, from

$\text{Ar (g, } p_1, V_1 \text{)} \text{ (initial)} \rightarrow \text{Ar (g, } P_2, V_2 \text{)} \text{ (final)}$; such that $V_1 > V_2$ and $p_1 < p_2$

Compression through two paths



1st Path:

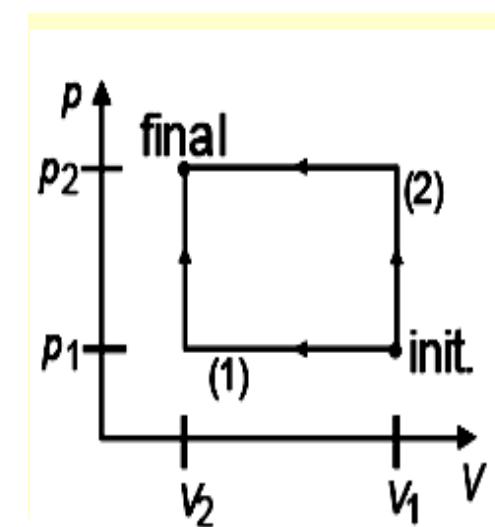
$\text{Ar(g, } p_1, V_1 \text{)} \rightarrow \text{Ar(g, } p_1, V_2 \text{)} \rightarrow \text{Ar(g, } p_2, V_2 \text{)}$

First $V_1 \rightarrow V_2$ when p held constant at p_1 ;
then $p_1 \rightarrow p_2$ when V held constant at V_2

2nd Path:

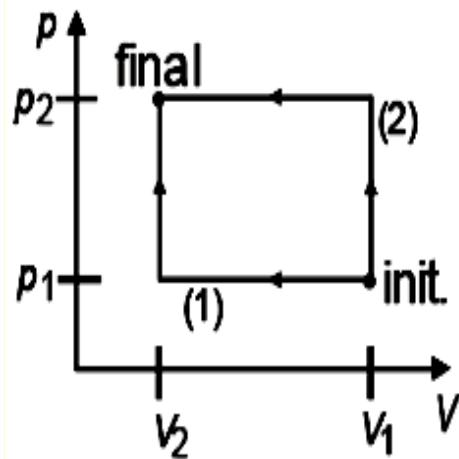
$\text{Ar(g, } p_1, V_1 \text{)} \rightarrow \text{Ar(g, } p_2, V_1 \text{)} \rightarrow \text{Ar(g, } p_2, V_2 \text{)}$

First $p_1 \rightarrow p_2$ when V held constant at V_1 ;
then $V_1 \rightarrow V_2$ when p held constant at p_2



Note for the closed cycle, total work = $w[\text{path (1)}] - [\text{path (2)}]$

Is Work a STATE FUNCTION?



$$w(1) = - \int_{V_1}^{V_2} p_{ext} dV - \int_{V_2}^{V_1} p_{ext} dV$$

$$w(1) = - \int_{V_1}^{V_2} p_1 dV = - p_1 (V_2 - V_1) = p_1 (V_1 - V_2)$$

$$w(2) = - \int_{V_1}^{V_2} p_{ext} dV - \int_{V_1}^{V_2} p_{ext} dV$$

$$w(2) = - \int_{V_2}^{V_1} p_2 dV = - p_2 (V_2 - V_1) = p_2 (V_1 - V_2)$$

NOTE:

- Work done on the system to compress it is NOT EQUAL through the two paths. i.e., $w(1) \neq w(2)$
- \therefore Net work done on the system in the complete cycle $\neq 0$
i.e., $[w(1) - w(2)] \neq 0$; $\oint \partial w \neq 0$ (closed cycle)
- This means w is NOT a state function \therefore we CAN NOT write $w = f(V, p)$

Energy, Work and Heat

Energy is the capacity to do work.

Energy classification into: \Rightarrow kinetic potential

(by motion) (by position)

Is purely arbitrary! e.g. thermal chemical, electrical

- Heat and work are NOT “types” of ENERGY, but are processes involving TRANSFER of energy.
 - They appear and disappear at the system boundary. They are path variables.
 - Heat is the transfer of energy from one body to another based on temperature difference. They are path variables.
 - Heat stimulates random motion.
 - Convention: if heat flows into the system, $q > 0$.
 - Work is the transfer of energy by some mechanism other than temperature difference.
 - They appear and disappear at the system boundary. They are path variables.
 - Convention: if work is done on the system, $w > 0$.
 - Work stimulates organized motion.
 - Work “degrades” into heat.
- Qualitative observations by Count Rumford (Ben Thompson)
- Quantitative measurements by James Joule

Energy

Concept of Internal Energy

- $E = K + V + U$ where, K and V are the macroscopic (not molecular) kinetic and potential energies of the system
- U is the internal energy of the body (due to molecular motions and intermolecular interactions)
- Internal Energy, U , is the total kinetic energy due to motion of molecules (translational, rotational, vibrational) the total potential energy associated with the vibrational and electric energy of atoms within molecules or crystals.
- $U_m = U_{tr, m} + U_{rot, m} + U_{vib, m} + U_{internal, m} + U_{rest, m}$ (where, $U_{rest, m}$ = rest mass energy of electrons & nuclei = $m_{rel}c^2$ = constant)
- U_m (molar internal energy) = U/n , where n = no. of moles of the substance

Energy

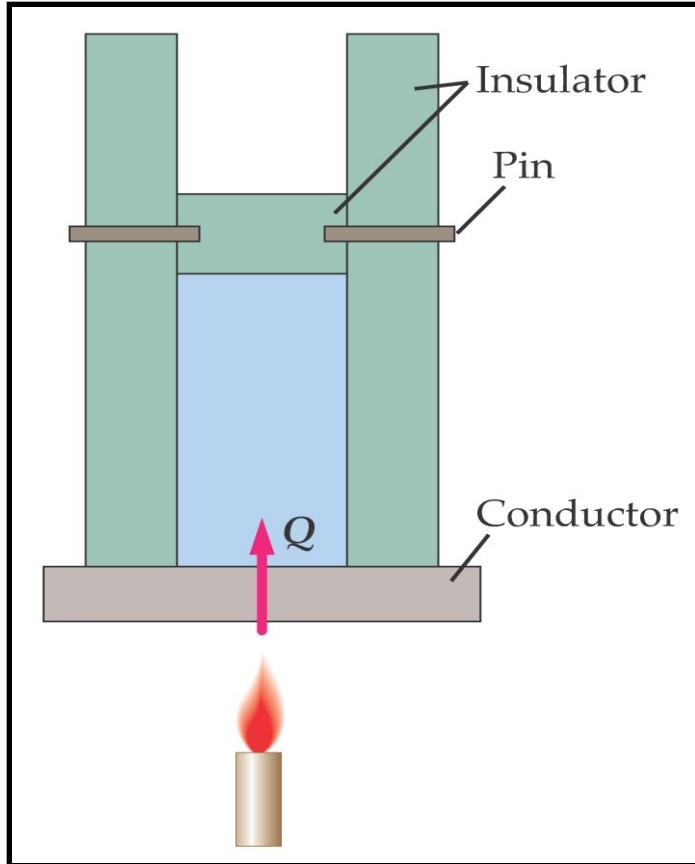
Properties of Internal Energy

- U is a State function, a property that: Depends only on the current state of the system and is independent of how or through path that state has been reached.
- It is an exact differential and its fundamental variables are V and T

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

- For cyclic process, $\oint dU = 0$
- U is an Extensive property

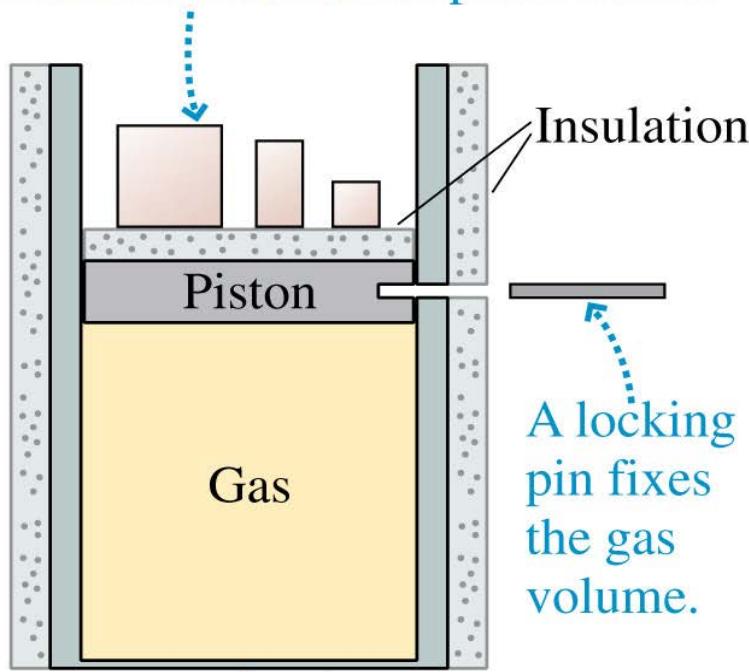
HEAT



- Heat is transferred between a system and surrounding by virtue of a *temperature difference only*.
- Heat is **not a state function** (path dependent).
- Heat can be transferred **reversibly or irreversibly**. A reversible transfer of heat requires the *temperature difference* between two bodies be *infinitesimal*.

WORK AND HEAT

Masses determine the gas pressure. Work is done as the masses move up and down.



Heat energy can be transferred into or out of the gas.



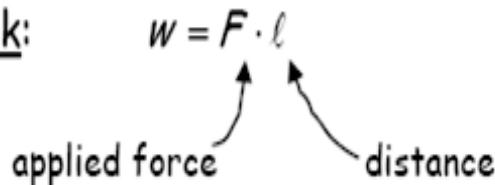
Flame



- For an **isochoric process**, insert the locking pin so the volume cannot change.
- For an **isothermal process**, keep the thin bottom in thermal contact with the flame or the ice.
- For an **adiabatic process**, add insulation beneath the cylinder, so no heat is transferred in or out.

WORK

- Work:



Expansion work, work of expansion (or compression)
Non-expansion / additional work / any other work

where $F = p_{ext}A$

**Work is required to move an object
a distance dz against an opposing
force F**

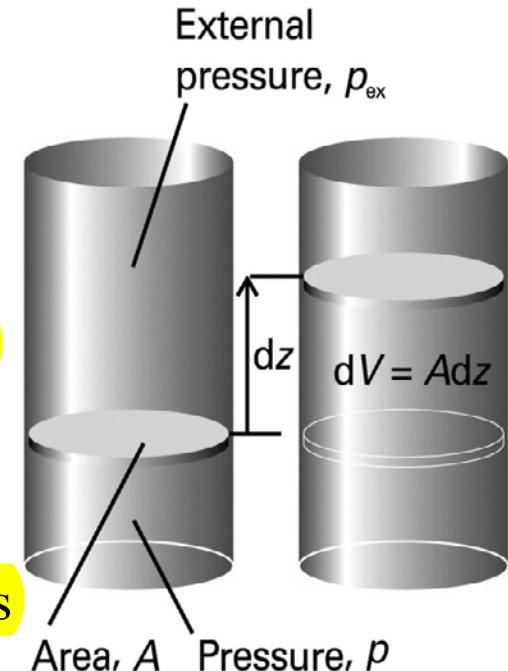
$$w = -(p_{ext}A)\ell = -p_{ext}\Delta V$$

Total work done,

$$w = - \int_{v_i}^{v_f} p_{ex} dV$$

- p_{ex} = external pressure
- A = piston area
- dz = displacement
- $dV = Adz$ = volume change for the gas

$$-\int_{V_i}^{V_f} p_{ex} dV = -\int_{V_i}^{V_f} pdV \rightarrow \text{Reversible process}$$



- Work done **on** the system →

$$0 < w$$

i.e., Compression

- Work done **by** the system →

$$w < 0$$

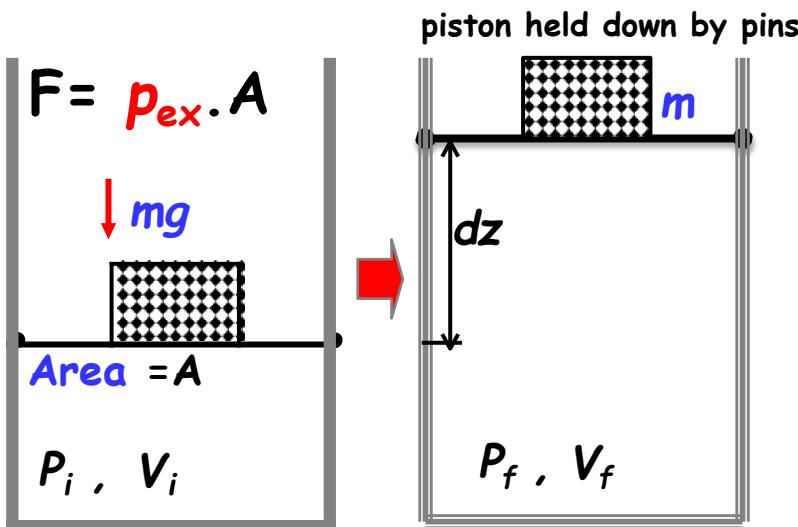
i.e., Expansion

WORK

- Expansive work, work of expansion (or compression)

$$F = mg$$

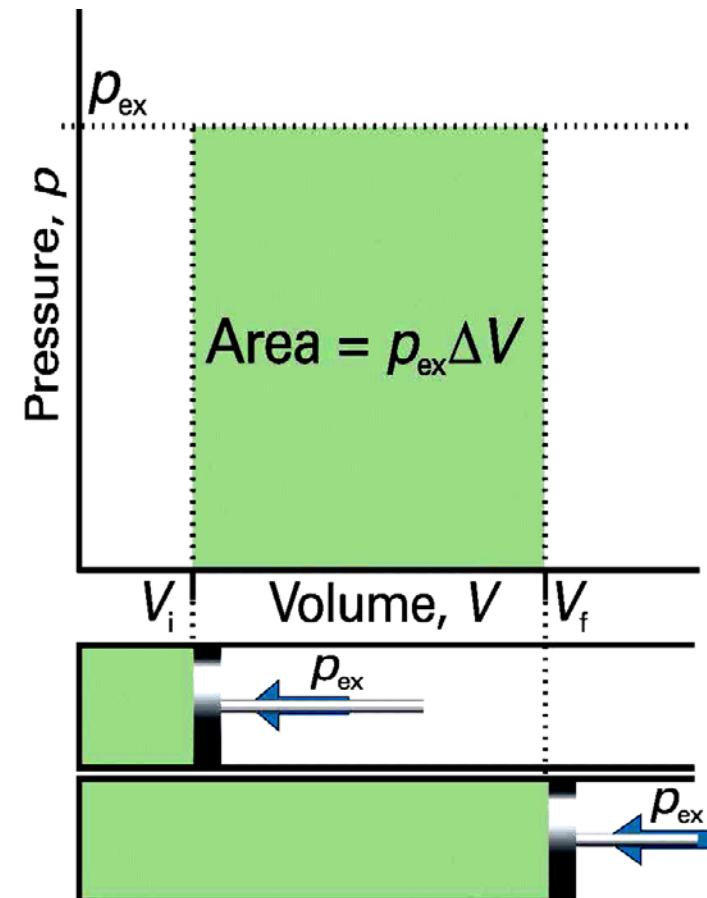
$$p_{ex} = mg/A$$



$$w = - F \cdot dz = mg \cdot dz$$

$$w = - p_{ex} \cdot A \cdot dz$$

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



- Work done **on** the system →

$$0 < w$$

i.e., **Compression**

- Work done **by** the system →

$$w < 0$$

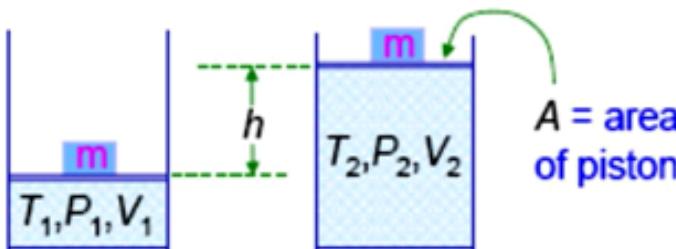
i.e., **Expansion**

Pressure–Volume Work 1

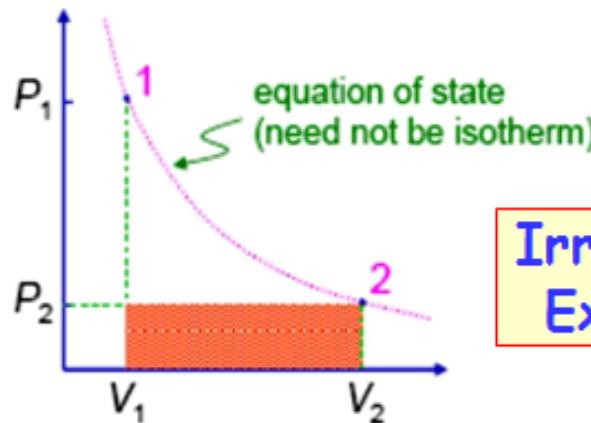
Expansion

$$P_1 > mg / A$$

$$0 \leq P_{ext} \leq P_2 \quad P_2 = P_{ex} = mg / A$$



$$\begin{aligned} w &= -(mg)h \\ &= -(P_{ex}A)h \\ &= -P_{ex}(V_2 - V_1) \end{aligned}$$



Expansion into a vacuum

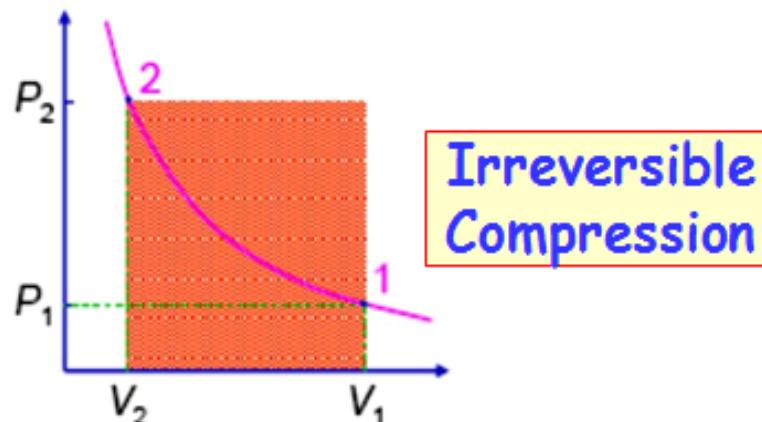
$$P_{ex} = 0 \Rightarrow w = 0$$

Compression

$$0 \leq P_{ext} \leq P_2 \quad P_1 < P_{ex}$$

$$P_2 = P_{ex}$$

$$w = -P_{ex}(V_2 - V_1)$$



Thus, **MORE WORK** has been **PRODUCED** in **MULTI stage EXPANSION** than in the single stage expansion

Expansion

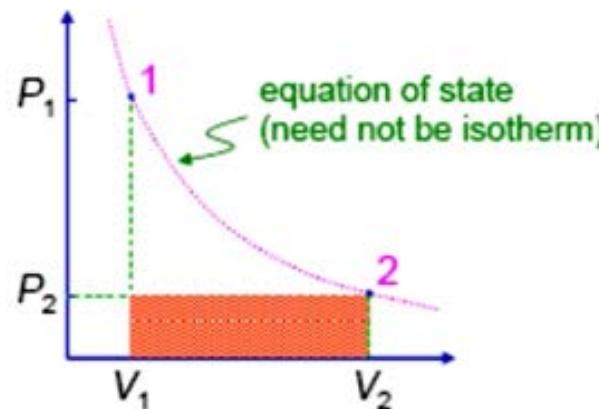
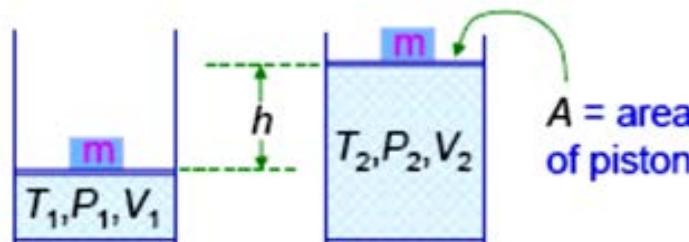
$$P_1 > mg / A$$

$$P_2 = P_{\text{ex}} = mg / A$$

$$w = -(mg)h$$

$$= -(P_{\text{ex}}A)h$$

$$= -P_{\text{ex}}(V_2 - V_1)$$

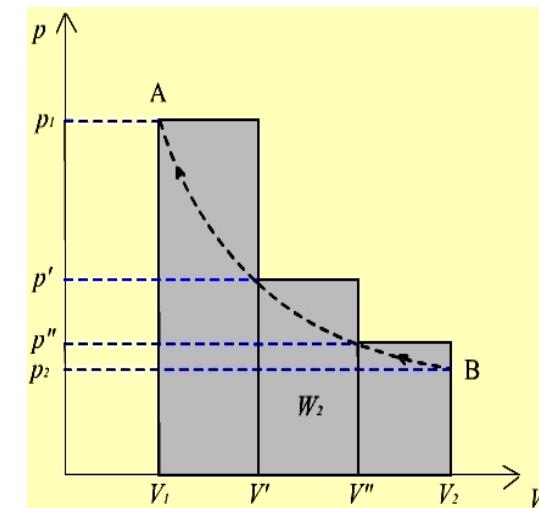
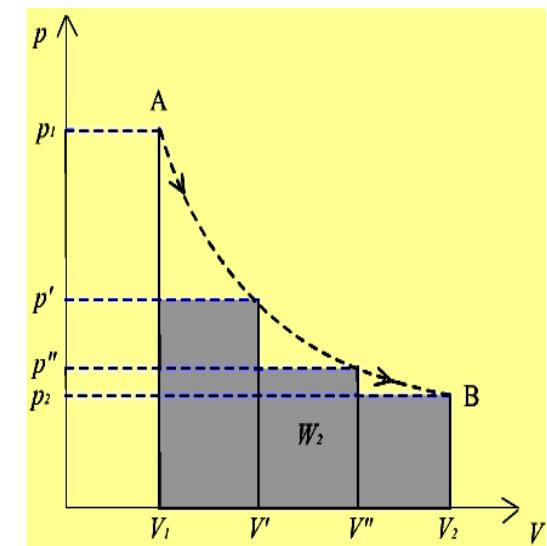
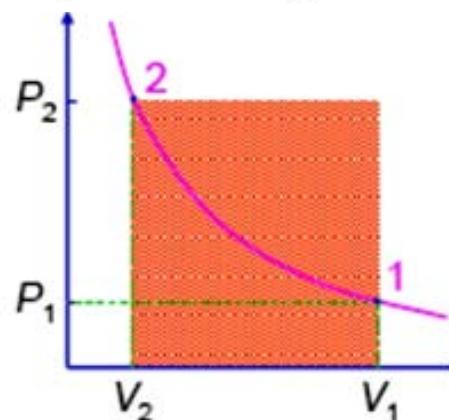


Compression

$$P_1 < P_{\text{ex}}$$

$$P_2 = P_{\text{ex}}$$

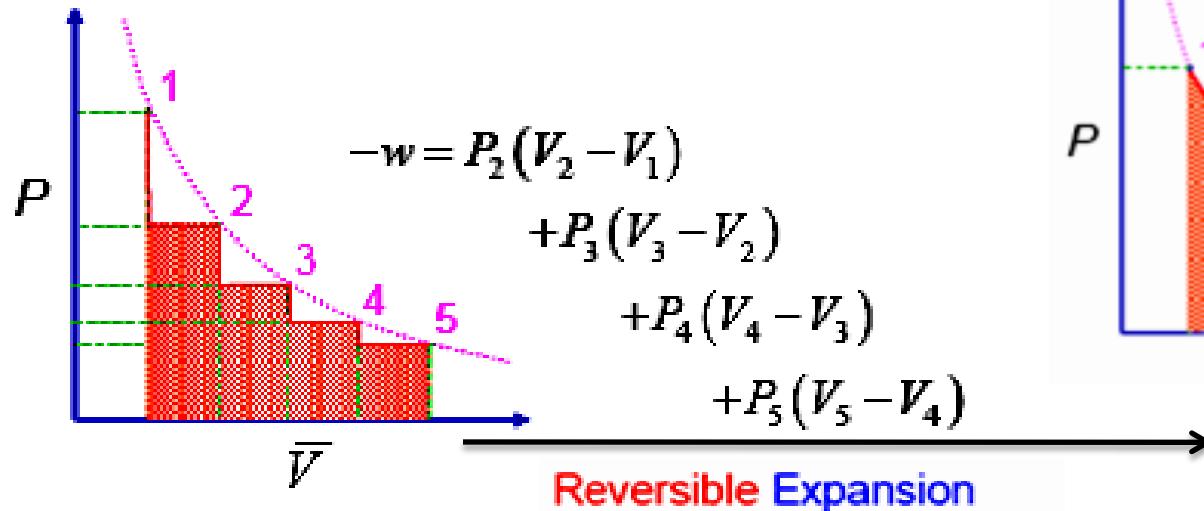
$$w = -P_{\text{ex}}(V_2 - V_1)$$



Thus, **LESS WORK** is **DESTROYED** in **MULTI stage COMPRESSION** than in the single stage compression

Multi-stage Expansion

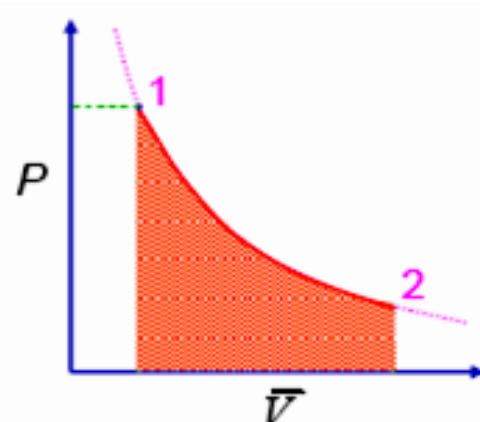
Multi-stage Expansion



Make steps so small that

$$dP \rightarrow 0, dV \rightarrow 0$$

Then $-\delta w = P_{ex} dV$



Therefore, the Maximum and Minimum quantity of Work = in a REVERSIBLE PROCESS

$$w = - \int_{v_i}^{v_f} p_{ex} dV$$

CONDITION FOR MAXIMUM WORK

- For **WORK to be MAXIMUM**,
 p_{ext} should possess the **LARGEST possible value** at each stage of the expansion process.
- This means, if the gas is to **EXPAND**, then p_{ext} must be **LESS than pressure of the gas inside the cylinder**, which let us say is p
- Therefore, the condition for obtaining the **maximum work should be**, $p_{ext} = p - dp$

$$w_{max} = - \int_{v_i}^{v_f} p_{ext} dV = - \int_{v_i}^{v_f} (p - dp) dV = - \int_{v_i}^{v_f} (pdV - dpdV)$$

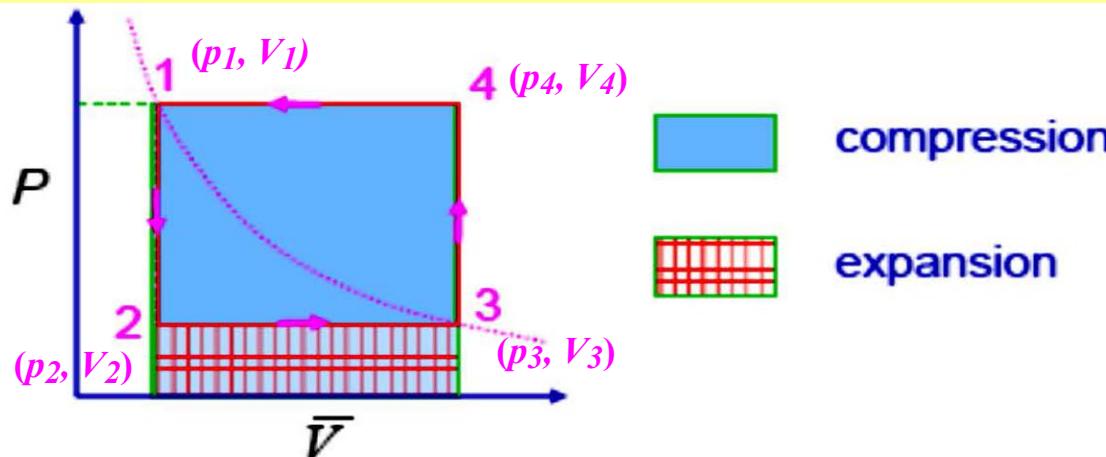
Neglecting infinitesimals of order higher than 1, we will get:

$$w_{max} = - \int_{V_i}^{V_2} pdV$$

For ideal gases $P = nRT/V$

and at fixed temperature $w_{rev} = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$

Pressure–Volume Work



Consider the cyclic path $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$

$$\begin{aligned}-w &= 0 + P_3(V_3 - V_1) + 0 + P_1(V_1 - V_3) \\ &= (P_3 - P_1)(V_3 - V_1)\end{aligned}$$

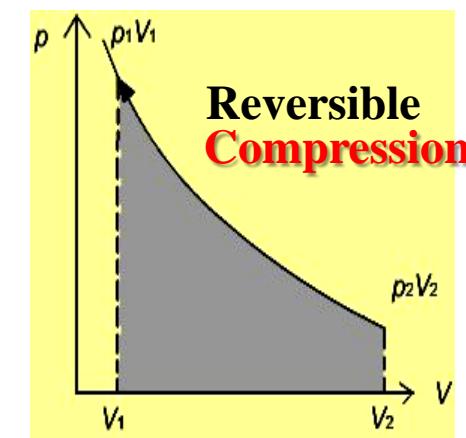
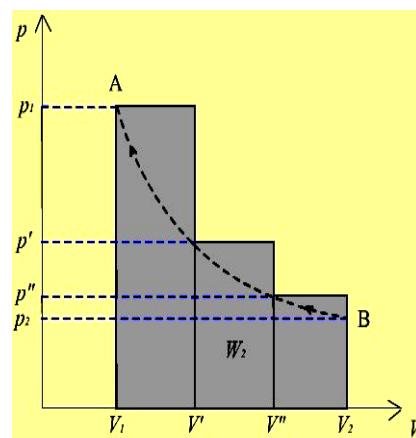
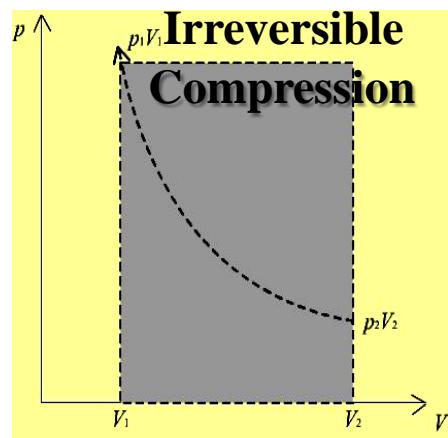
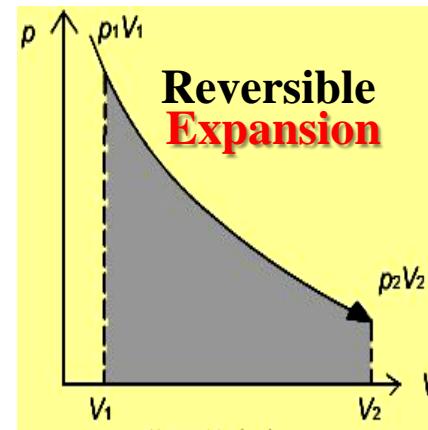
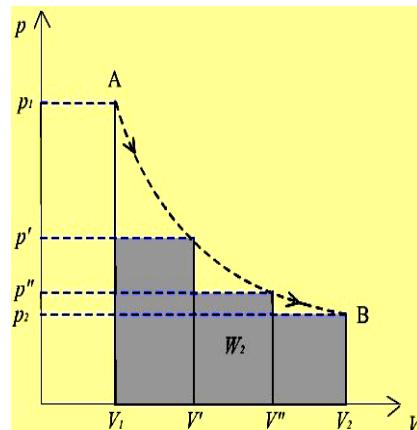
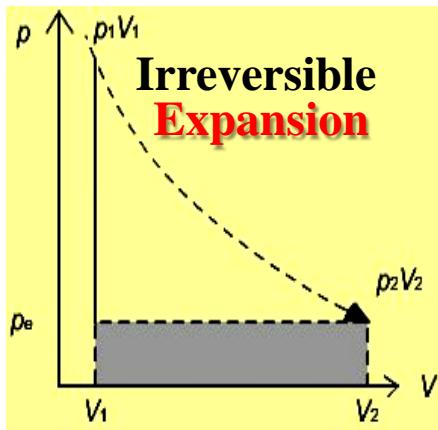
Consider the cyclic reversible path $1 \rightarrow 3 \rightarrow 1$

$$\begin{aligned}-w &= \int_{V_1}^{V_3} P dV + \int_{V_3}^{V_1} P dV \\ &= \int_{V_1}^{V_3} P dV - \int_{V_1}^{V_3} P dV = 0\end{aligned}$$

Even for a cyclic process w depends on path

$$\oint dU = 0 \quad \Leftrightarrow \quad -\oint \delta w = \oint \delta q$$

REVERSIBLE AND IRREVERSIBLE WORK



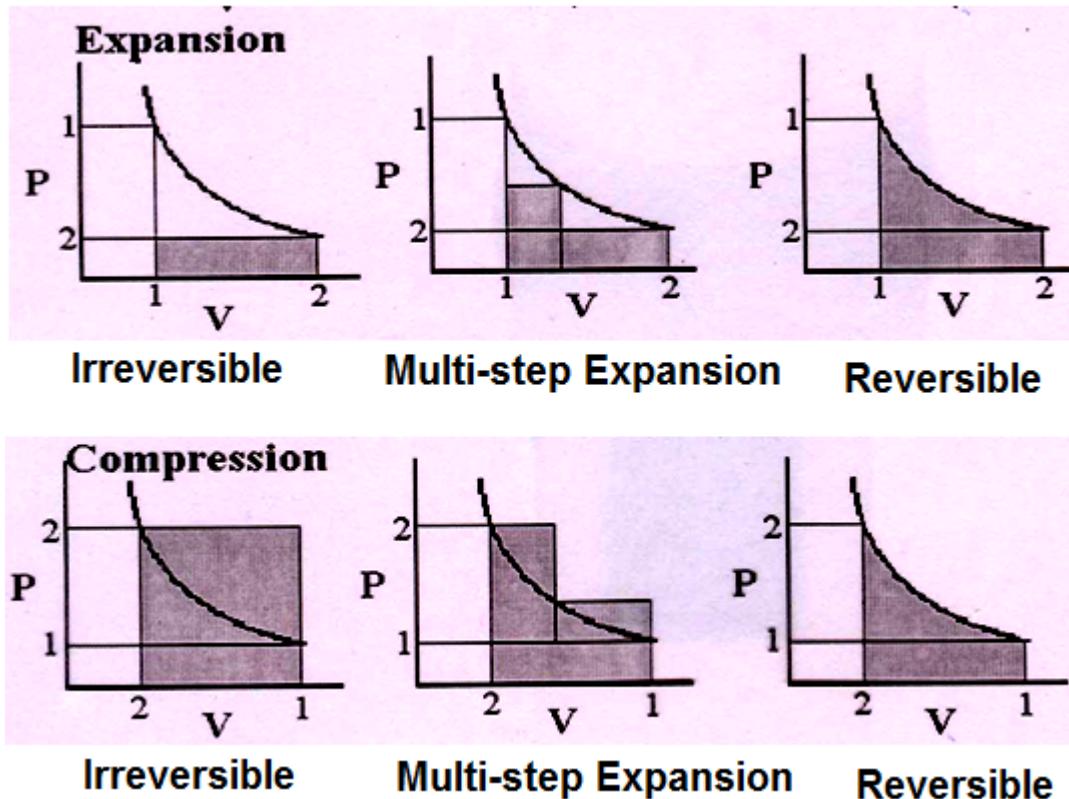
For a Reversible Process:

- Work on Expansion = Work on Compression (for the same path)

For an Irreversible Process:

- Work on Expansion (is less than) \neq Work on Compression (for the same path)

REVERSIBLE AND IRREVERSIBLE WORK



- Work done on expansion by the system on surroundings (sign negative) operating between specified initial and final states and passing through and specified path is maximum work available from a system when the changes take place reversibly

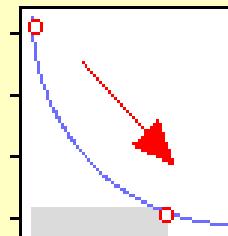
$$|W_{rev}| > |W_{irrev}|$$

- Work is a path dependent parameter, path function (so as Heat)

Solved Example

2.24 L, 10 atm \longleftrightarrow 22.4 L, 1 atm

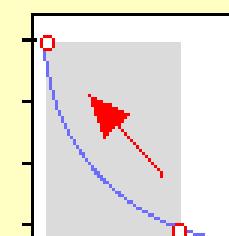
Expansion



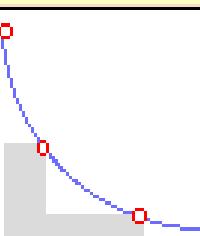
1 stage

-20 L-atm

Compression

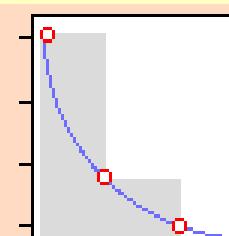


+202 L-atm

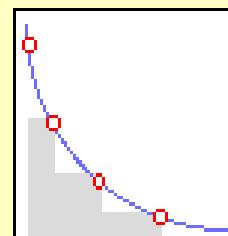


2 stages

-28 L-atm

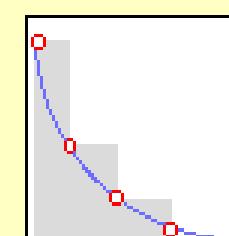


+119 L-atm



3 stages

-33 L-atm



+85 L-atm

infinite stages
(reversible)

P

-52 L-atm

(maximum work)

+52 L-atm

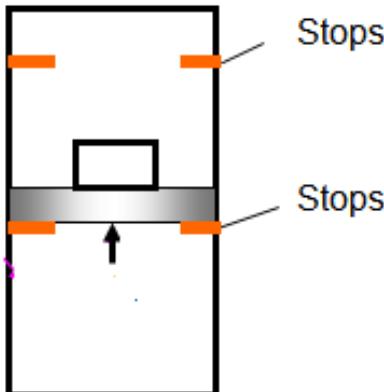
(minimum work)

P

$$\nabla |w_{\text{rev}}(\text{compression})| = |w_{\text{rev}}(\text{expansion})| \nabla$$

WORK: Irreversible

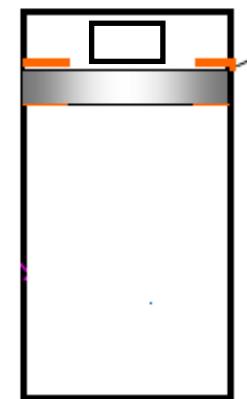
Initial volume and final volume SAME



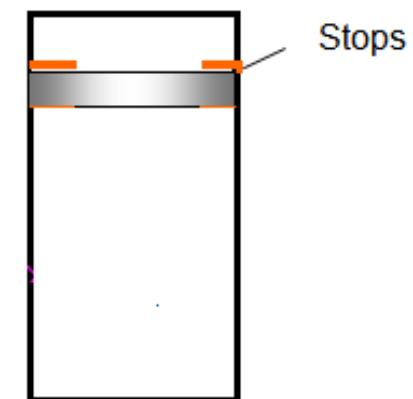
Initial condition



Case I



Case II



Case III

Work done in each case? All are Irreversible form of Work

Case I : Mass removed – system allowed to reach equilibrium.

$$p_{ex} = p_f ; \quad w = -p_f \Delta V$$

Case II : System expansion restricted

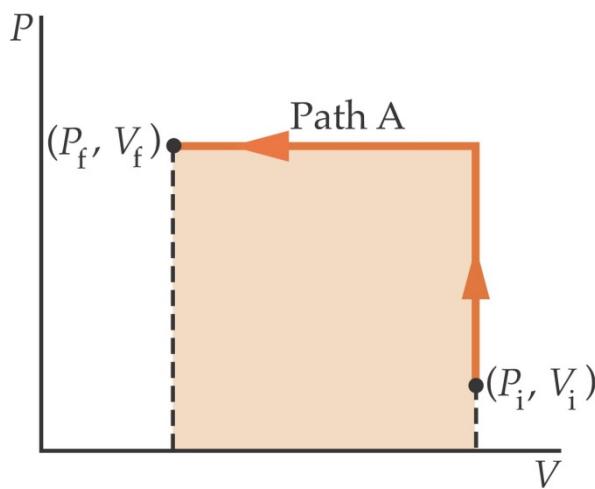
$$p_{ex} < p_i ; \quad w = -p_{ex} \Delta V$$

Case III: Expansion against vacuum $p_{ex} = 0 ; \quad w = 0$

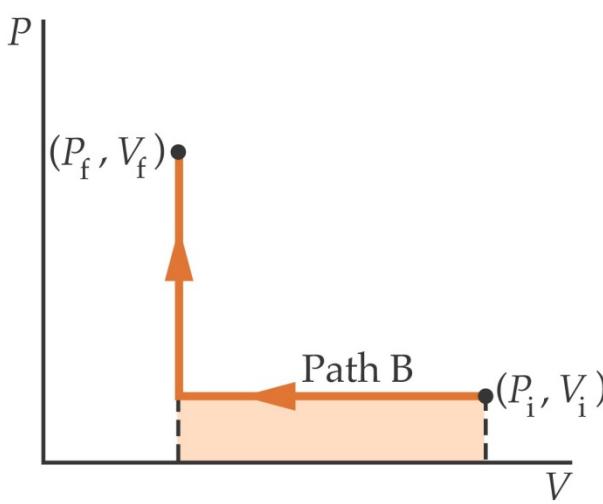
WORK: P-V diagrams

P-V diagrams:

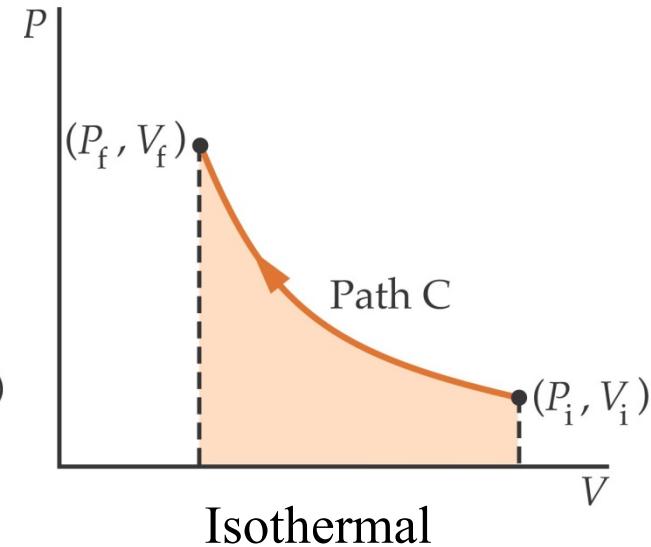
Connecting an initial state and a final state by three paths



Constant pressure



Constant Volume

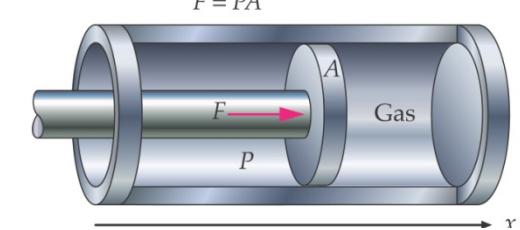


Constant Temperature

$$W_{\text{on gas}} = - \int_{V_1}^{V_2} P dV = P(V_1 - V_2)$$

$$W_{\text{on gas}} = - \int_{V_1}^{V_2} P dV = 0$$

$$W_{\text{on gas}} = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1}$$



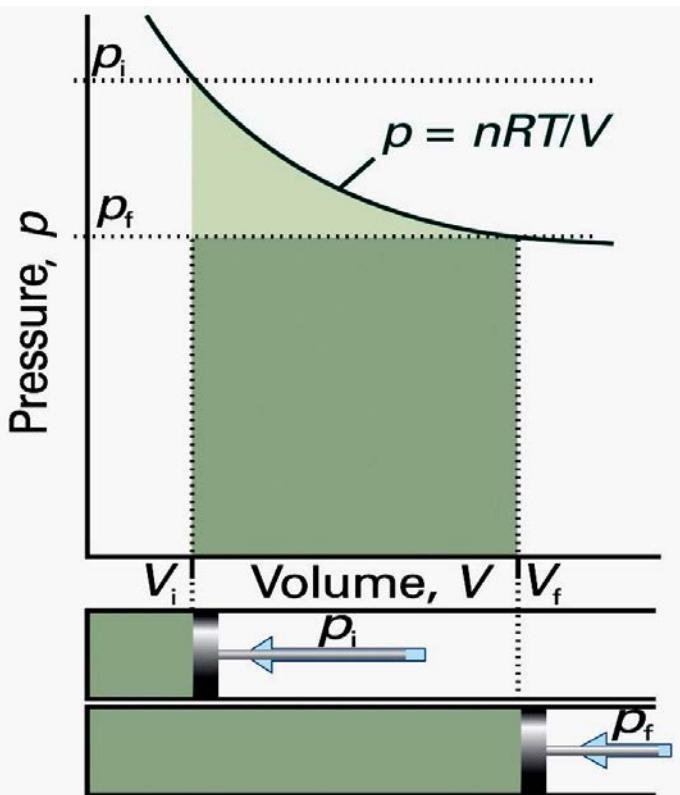
WORK EXPRESSIONS

Reversible Isothermal Expansion :

$$w_{max} = - \int (p_{ex} - dp) dV = - \int (pdV - dpdV)$$

$$w_{max} = - \int pdV = w_{rev}$$

when, $p = p(V)$ and $p = nRT/V$ for ideal gas



$$w_{rev} = -nRT \int_{V_i}^{V_f} \left(\frac{dV}{V} \right) = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$w_{rev} = nRT \ln \left(\frac{p_f}{p_i} \right)$$

- At higher T , work done is more for same expansion of volume.

- Maximum work is obtained when expansion is reversible.

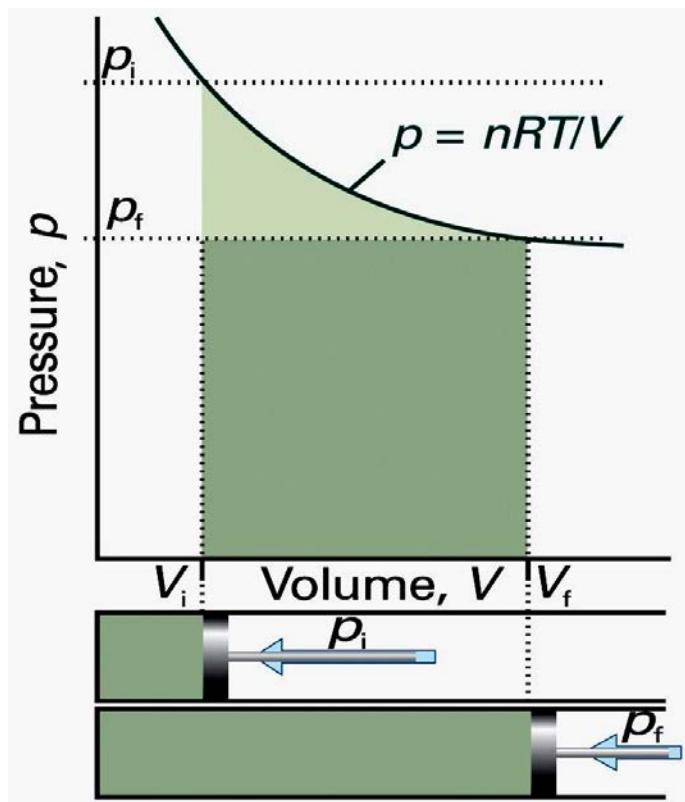
Irreversible Isothermal Expansion:

$$w_{irrev} = -p_{ex} \int_{V_i}^{V_f} dV \equiv -p_{ex} (V_f - V_i) = -p_{ex} \Delta V$$

WORK: SUMMARY

Reversible Isothermal Expansion :

when, $p = p(V)$ and $p = nRT/V$ for ideal gas



$$w_{max} = - \int (p_{ex} - dp)dV = - \int (pdV - dpdV)$$

$$w_{max} = - \int pdV = w_{rev}$$

$$w_{rev} = -nRT \int_{V_i}^{V_f} \left(\frac{dV}{V} \right) = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

Irreversible Isothermal Expansion:

$$w_{irrev} = -p_{ex} \int_{V_i}^{V_f} dV \equiv -p_{ex}(V_f - V_i) = -p_{ex} \Delta V$$

Free Expansion:

$$p_{ext} = 0 \rightarrow w = 0$$

Expansion against constant final pressure:

$$w = -p_f(V_f - V_i)$$

Expansion, i.e., $V_f > V_i$, $w < 0$ (Work Done by the System on Surrounding)

Compression, i.e., $V_f < V_i$, $w > 0$ (Work Done on the System by Surrounding)

SUMMARY OF WORK EXPRESSIONS

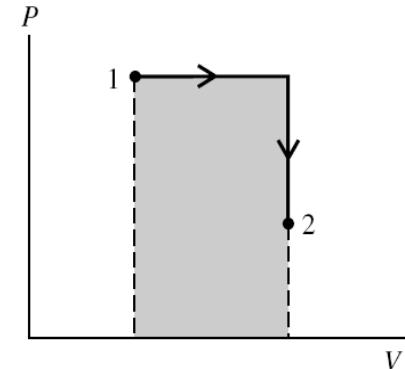
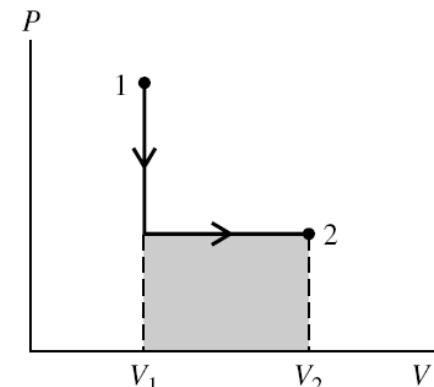
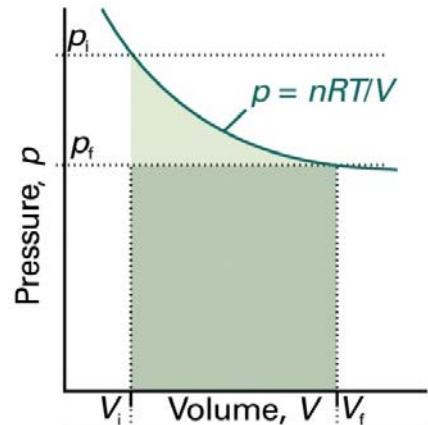
Irreversible Work	$w = - p_{ex} \Delta V$
Irreversible Work (Free Expansion)	$w = 0$ Zero External Pressure
Reversible Work	$w = - \int p \, dV$
Reversible Work at constant V (ex: <i>bomb calorimeter</i>)	$w = 0$
Reversible Work at constant p (ex: <i>heating at const p, phase transition</i>)	$w = - p \Delta V$
Reversible Work (Ideal Gas)	$w = - \int \frac{nRT}{V} \, dV$
Reversible Isothermal Work (Ideal Gas)	$w = -nRT \ln \frac{V_f}{V_i}$; $w = nRT \ln \frac{p_f}{p_i}$
Reversible Work (van der Waal Gas)	$w = - \int \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2} \right) dV$
Reversible Isothermal Work (van der Waal Gas)	$w = -nRT \ln \frac{V_2-nb}{V_1-nb} + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$
Reversible Adiabatic Work	$w = - \int pdV = C_V dT$
Irreversible Adiabatic Work	$w = - p \Delta V = C_V \Delta T$

Work is Path Dependent: Assignment

Ideal gas, closed system, reversible process

Calculate w_f and w_b

- 10 Pa, 1 m³, $T \xrightarrow{\text{isothermal}} 1 \text{ Pa}, 10 \text{ m}^3, T$
- 10 Pa, 1 m³, $T \xrightarrow{\text{isochoric}} 1 \text{ Pa}, 1 \text{ m}^3, T_2 \xrightarrow{\text{isobaric}} 1 \text{ Pa}, 10 \text{ m}^3, T$
- 10 Pa, 1 m³, $T \xrightarrow{\text{isobaric}} 10 \text{ Pa}, 10 \text{ m}^3, T_3 \xrightarrow{\text{isochoric}} 1 \text{ Pa}, 10 \text{ m}^3, T$



w_{rev} depends on the path used to go from 1 to 2, and w_{rev} can have *any* positive or negative value for a given change of state

WORK: Assignment

25 L of gas is enclosed in a cylinder/piston apparatus at 2 atm of pressure and 300 K. A 100 kg of mass is placed on the piston causing the gas to compress to 20 L at constant pressure. This is done by allowing heat to flow out of the gas.

- What is the work done on the gas?
- What is the change in internal energy of the gas?
- How much heat flowed out of the gas?

- $P_o = 202,600 \text{ Pa}$, $V_o = 0.025 \text{ m}^3$,
- $T_o = 300 \text{ K}$, $P_f = 202,600 \text{ Pa}$,
- $V_f = 0.020 \text{ m}^3$, $T_f = ?$
- $n = PV/RT$ $W = -P\Delta V$ $\Delta U = 3/2 nR \Delta T$

$$W = -P\Delta V = -202,600 \text{ Pa} (0.020 - 0.025) \text{ m}^3$$

= 1013 J energy added to the gas

$$\Delta U = 3/2 nR \Delta T = 1.5(2.03)(8.31)(-60) = -1518 \text{ J}$$

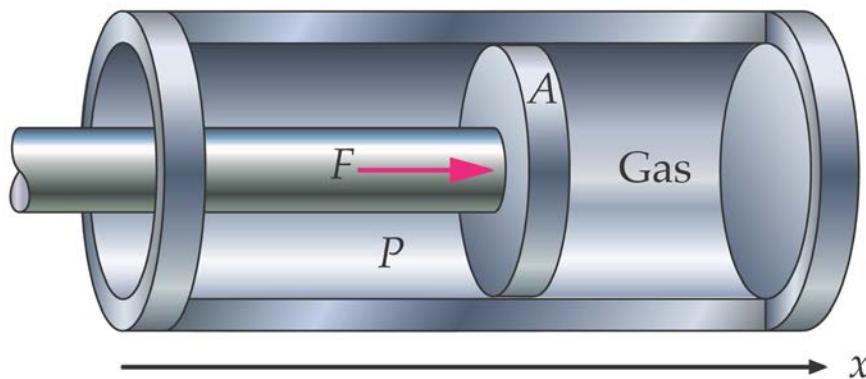
$$Q = -505 \text{ J}$$

WORK: Assignment

A gas confined in a cylinder with a movable piston

Work done on the system, W_{on} , is the energy transferred as work to the system. When this energy is added to the system its value will be positive.

$$F = PA$$



The work done on the gas in an expansion is

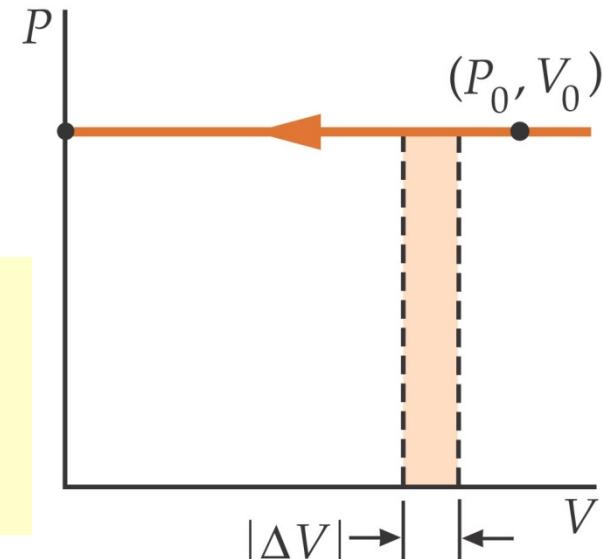
$$W_{\text{on gas}} = - \int_{V_1}^{V_2} P dV$$

$$W_{\text{on gas}} = -W_{\text{by gas}}$$

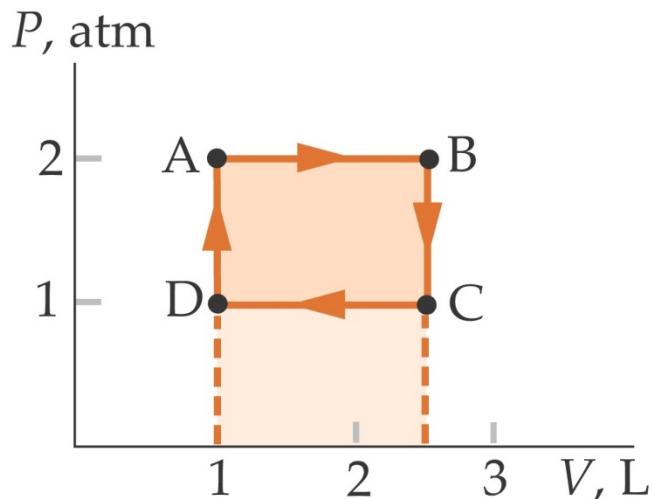
P-V diagrams Constant pressure

$$W_{\text{on gas}} = - \int_{V_1}^{V_2} P dV = P(V_1 - V_2)$$

If 5 L of an ideal gas at a pressure of 2 atm is cooled so that it contracts at constant pressure until its volume is 3 L what is the work done on the gas? [405.2 J]

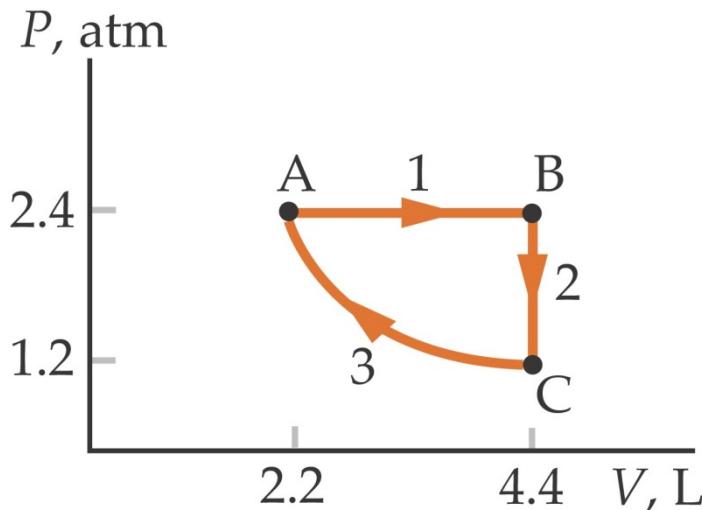


WORK: Assignment



A diatomic ideal gas undergoes a cycle starting at point A (2 atm, 1L). Process from A to B is an expansion at constant pressure until the volume is 2.5 L, after which, it is cooled at constant volume until its pressure is 1 atm. It is then compressed at constant pressure until the volume is again 1L, after which it is heated at constant volume until it is back to its original state. Find (a) the work, heat and change of internal energy in each process (b) the total work done on the gas and the total heat added to it during the cycle.

WORK: Assignment



A system consisting of 0.32 mol of a monoatomic ideal gas occupies a volume of 2.2 L, at a pressure of 2.4 atm. The system is carried through a cycle consisting:

1. The gas is heated at constant pressure until its volume is 4.4L.
2. The gas is cooled at constant volume until the pressure decreases to 1.2 atm
3. The gas undergoes an isothermal compression back to its initial point.
 - (a) What is the temperature at points A, B and C
 - (b) Find W, Q and ΔU for each process and for the entire cycle

The Laws of Thermodynamics

First Law of Thermodynamics

Law of Conservation of Energy

- A system can contain *only internal energy*.
 - A system does not contain **heat** or **work**.
 - These only occur during a *change* in the system. The sum of the heat, q , transferred to a system and the work, w , performed **on** it equals to the total change in the system's internal energy, dU

$$dU = \partial q + \partial w$$

- When energy passes, as work, as heat, or with matter, into or out from a system, the system's internal energy changes in accord with the law of conservation of energy.
- Equivalently, **perpetual motion machines of the first kind** are **impossible**. A hypothetical machine that can do/ produce work indefinitely without an energy source / without the input of energy. It thus violates the first law of thermodynamics: the law of conservation of energy.

Adiabatic process $\rightarrow dw = dU$

Cyclic Process

$$\oint dU = 0$$

First Law of Thermodynamics

- There exists an extensive state function U such that for any closed system,

$$\Delta U = q + w$$

Process	Sign convention
Transfer of heat to the system from the surrounding	$q > 0$
Transfer of heat from the system to the surrounding	$q < 0$
Expansion of system against an external pressure	$w < 0$
Compression of system by an external pressure	$w > 0$

First Law of Thermodynamics

- For an infinitesimal change in state,

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

- For an isolated system $\delta q = \delta w = 0 \Rightarrow dU = 0$
- For an adiabatic process $\delta q = 0 \Rightarrow dU = \delta w$
- For a cyclic process $\Delta U = \oint dU = 0 \Rightarrow q + w = 0$

The First Law of Thermodynamics: Work, Heat & Energy

Joule showed that it's possible to raise the temperature of H₂O

(a) with only heat

$$T_1 \rightarrow T_2$$



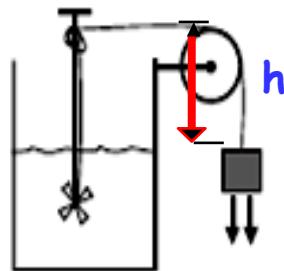
It is possible to have a change of state

$$(p_1, V_1, T_1) = (p_2, V_2, T_2)$$

or adiabatically (without heat transferred)
or nonadiabatically.

T₁ → T₂

(b) with only work
(weight falls &
churns propeller)



Historically measured in calories

[1 cal = heat needed to raise 1 g H₂O 1°C,
from 14.5°C to 15.5°C]

The modern unit of heat (and work) is the Joule.

Joule Heat Equivalent Experiment

$$1 \text{ cal} = 4.184 \text{ J}$$

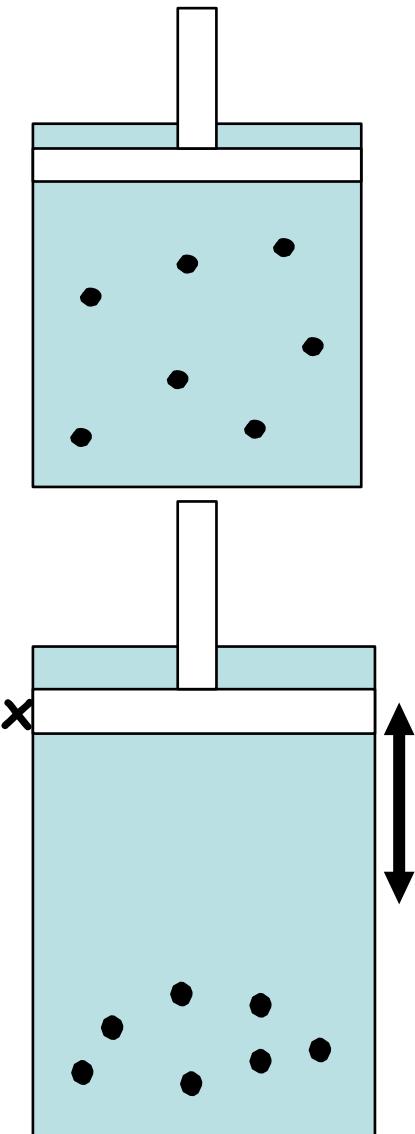
Joule Equivalent of Heat: 1 cal = 4.184 J

1st Law of Thermodynamics

Consider an example system of a piston and cylinder with an enclosed dilute gas characterized by P,V,T & n.

What happens to the gas if the piston is moved inwards? **Compression**

- If the container is insulated the temperature will rise, the atoms move faster and the pressure rises.
- Is there more internal energy in the gas? **Yes**
External agent did work in pushing the piston inward.
 $w = -F \times d = -(PA) \times (-\Delta x)$
w = PΔV
- Work done on the gas equals the change in the internal energy of the gas: **w = ΔU**



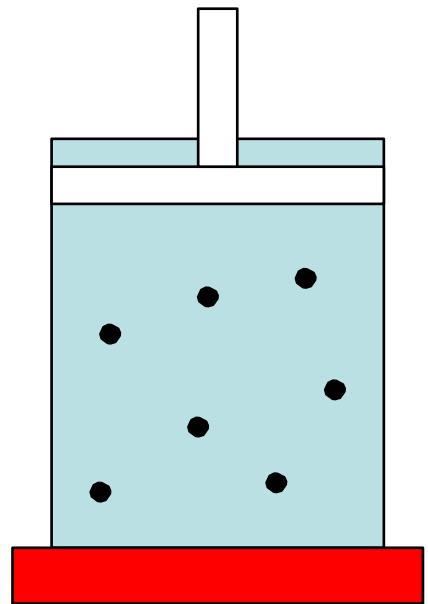
1st Law of Thermodynamics

- Change the situation:
- Keep the piston fixed at its original location.
- Place the cylinder on a hot plate.

What happens to gas?

- Heat flows into the gas.
- Atoms move faster, internal energy increases.
- Q = heat (in Joules) flows in
 ΔU = change in internal energy in Joules.

$$Q = \Delta U$$

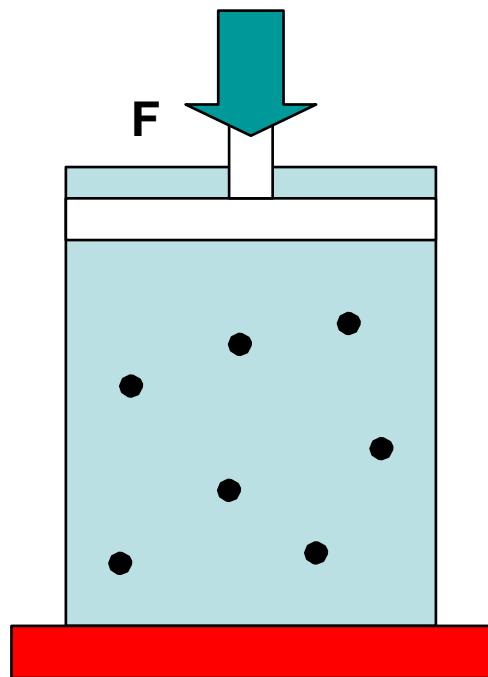


1st Law of Thermodynamics

What if we **added heat** and **pushed the piston in** at the same time?

- Work is done **on** the gas,
- Heat is added **to** the gas and
- the **internal energy** of the gas **increases**:

$$\Delta U = w + Q$$

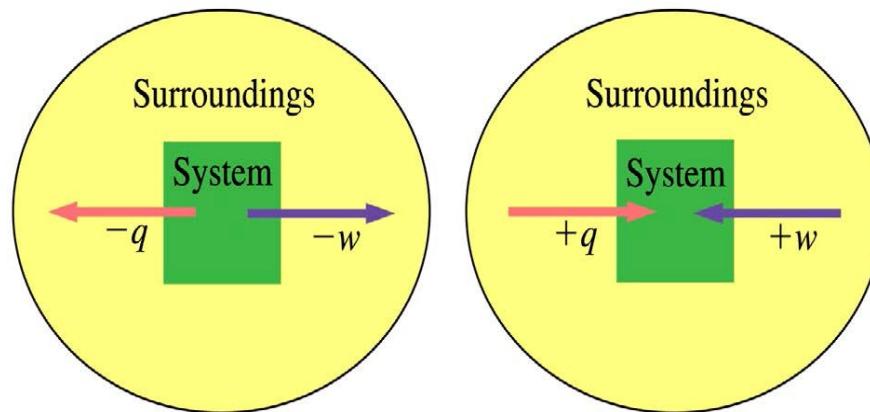


ΔU INCREASES with INCREASE in TEMP. of the system, when:

1. work is done **on** the system by the surrounding or,
2. heat flows **into** the system from the surrounding or,
3. both, **heat and work flows** from the surr. **into** the system

1st Law of Thermodynamics: Sign convention

- Work done **on** the system by surr \rightarrow + ve i.e., Compression
- Work done **by** the system on surr \rightarrow - ve i.e., Expansion



Alternate Statement: If a system is subjected to a CYCLIC transformation the work produced in the surroundings is EQUAL to the heat withdrawn from the surroundings.

$$Q = -w \text{ (change in } U \text{ is zero as it's a State function)}$$

If w is +ve (compression, work done on the system) then q will be -ve (heat will be released by the system) and vice versa

Heat Transactions and Heat Capacity:

In general change in the internal energy of a closed system is given by

- For $dV = 0$; $dw_{\text{exp}} = 0$ and if $dw_{\text{add}} = 0$, then

$$dU = dq \text{ (constant volume, no additional work)} = dq_V$$

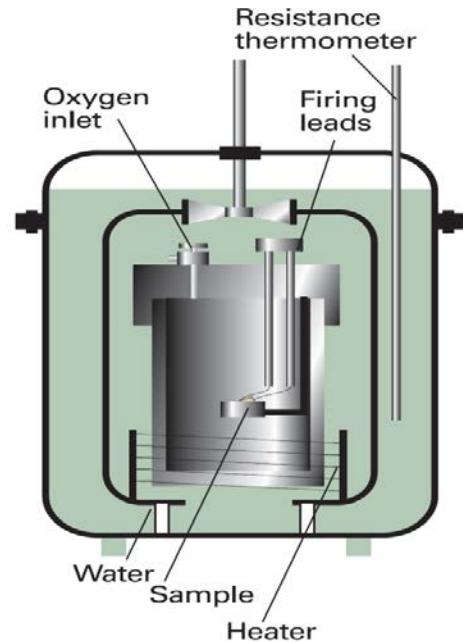
For a measurable change $\Delta U = q_V$

- **Heat Capacity, C** , the ratio of the heat supplied to the temperature rise it causes. $C = dq/dT$; $C = q / \Delta T$
- **Heat Capacity at Constant Volume, $C_V = (\partial U / \partial T)_V$**

- **Molar Heat Capacity**, the heat capacity divided by the amount of substance, $C_m = C / n$ (unit: $JK^{-1}mol^{-1}$)
- **Specific Heat Capacity**, the heat capacity divided by the mass, $C_s = C / m$ (unit: $JK^{-1}gm^{-1}$)

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

Measurement of ΔU

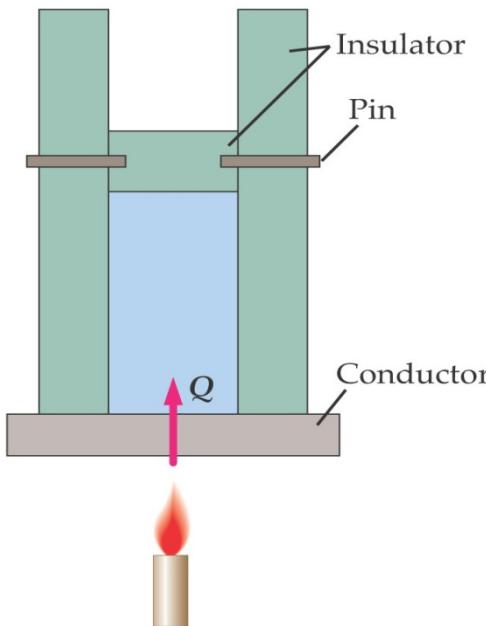


Adiabatic bomb calorimeter

Heat Capacity at Constant Volume and Internal Energy

- Variation with temperature at constant volume

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



If heat is added at constant volume,
no work is done.

Thus the heat added alone
contributes to the increase in
internal energy

C_V is a response function of the system. For a given quantity of heat, supplied to TWO substances, lower temperature change will be observed for the system having LARGER Heat Capacity

Heat Capacity at Constant Pressure and Enthalpy:

In general change in the internal energy of a closed system is given by

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

For $dV \neq 0$; $dw_{\text{exp}} \neq 0$; Even if $dw_{\text{add}} = 0$, $dU \neq dq$

By Definition: $H = U + pV$

- Properties of H :

✓ state function, $\Delta H = H_2 - H_1$ for change in state from 1 to 2

✓ exact differential

$$dH = d(U + pV) = dU + pdV + Vdp$$

✓ For constant pressure processes,

$$dp = 0 \Rightarrow dH = dU + pdV = \delta q_p \quad (\text{Using 1st law}) \quad (dU = \delta q - pdV)$$

For a finite isobaric process,

$$\int_1^2 dH = \Delta H = H_2 - H_1 = \int_1^2 \delta q_p = Q_p$$

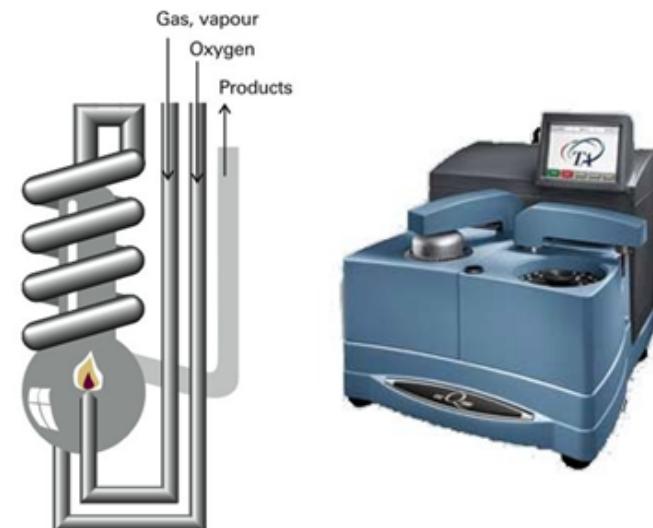
$$\Delta H = Q_p$$

Heat Capacity at Constant Pressure and Enthalpy:

- $H = U + pV$ and $\Delta H = Q_p$

Enthalpy changes are measured using

- isobaric calorimeter
- differential scanning calorimeter
- adiabatic flame calorimeter



Molar specific heat at constant pressure, $C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p$
At constant p , $dH = dq_p$ (constant pressure, no additional work)

$$dH = nC_p dT \quad \text{or,} \quad dH = C_{p,m} dT$$

In several experimental measurements,

$$C_{p,m} = f(T) = a + bT + \frac{c}{T^2} \Rightarrow$$

$$\Delta H = Q_p = n \int_{T_1}^{T_2} C_{p,m} dT$$

Heat Capacity at Constant Pressure and Enthalpy:

Variation of heat capacity over a wide range of temperature is given as:, $C_{p,m} = a + bT + c/T^2$ (Empirical expression)

$$dH = C_p dT = (a + bT + cT^2) dT$$

$$\int_{H_1}^{H_2} dH = \alpha \int_{T_1}^{T_2} dT + b \int_{T_1}^{T_2} T dT + c \int_{T_1}^{T_2} \left(\frac{1}{T^2}\right) dT$$

$$\Delta H = a(T_1 - T_2) + \frac{b}{2} a(T_1 - T_2) - c \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

This expression for ΔH is perfectly general and is valid for any transformation at constant P PROVIDED NO PHASE CHANGE or CHEMICAL REACTION occurs.

In case of a Transformation where phase change occurs:

Example: Vaporization of liquid at constant T and P

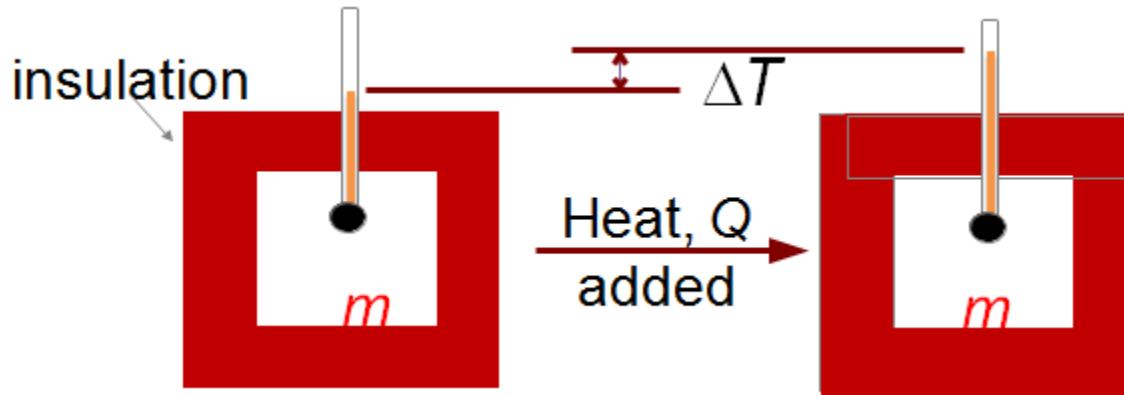
$$Q_{vap} = Q_p = \Delta H_{vap}$$

$$\text{Similarly, } Q_{fusion} = Q_p = \Delta H_{fus}$$

Example: Calculate ΔH for heating 1 gm of ice at 0°C to vapor at 100°C under 1 atm pressure.

$$\Delta H = \Delta H_{fus} + C_p \int_{273}^{373} dT + \Delta H_{vap}$$

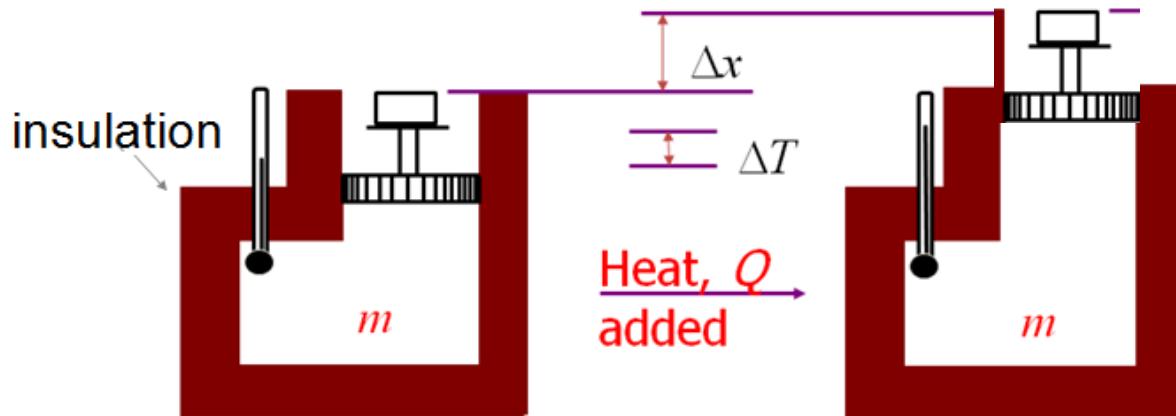
Heat Capacity for Constant Volume Processes (C_v)



- Heat is added to a substance of mass m in a **fixed volume** enclosure, which **causes a change in internal energy**, U . Thus,

$$Q = U_2 - U_1 = \Delta U = m C_V \Delta T$$

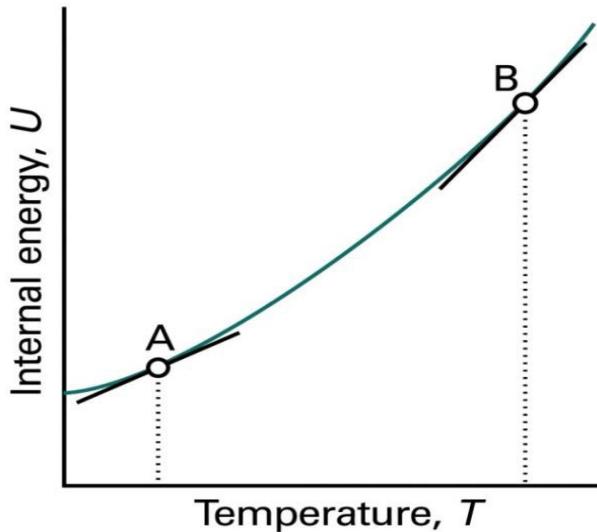
Heat Capacity for Constant Pressure Processes (C_p)



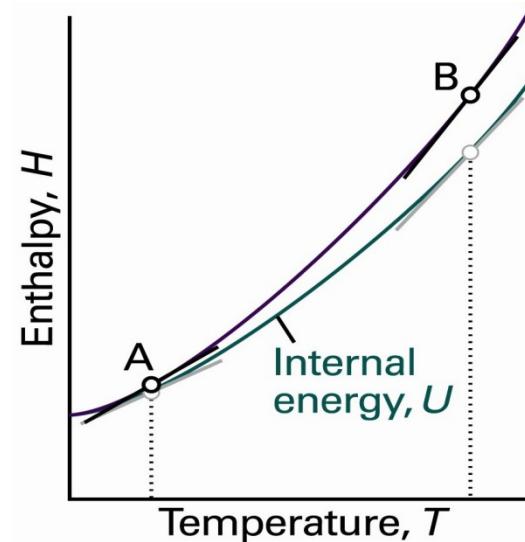
$$\bullet \quad C_p > C_V$$

- Heat is added to a substance of mass m held at a **fixed pressure**, which **causes a change in internal energy, U , and some PV work**.

Heat Transactions and Heat Capacity:



- The internal energy of a substance increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present suppose that the sample is a gas in a container of fixed volume.
- The slope of the tangent to the curve at any temperature is called the **Heat Capacity at Constant Volume** at that temperature.
- Note that the heat capacity is greater at B than at A



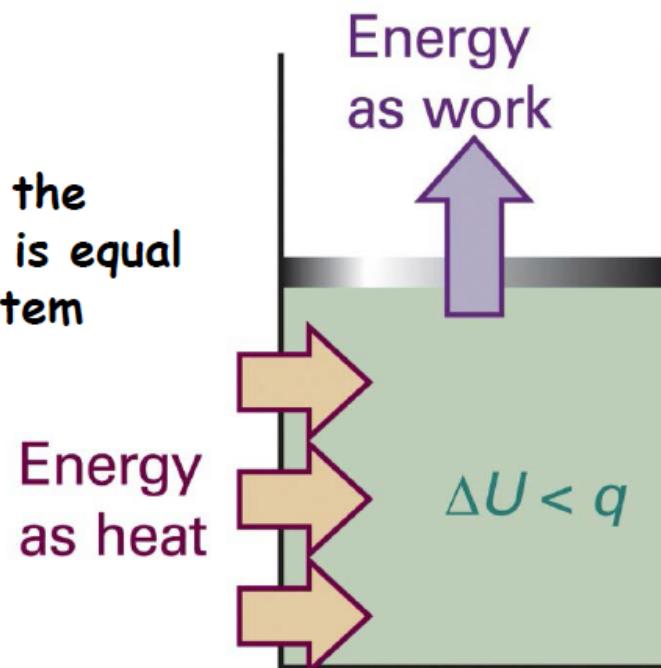
- The slope of the tangent to a curve of the enthalpy of a system subjected to a constant pressure plotted against temperature is the **Heat Capacity at Constant Pressure**.
- The slope may change with temperature, in which case the heat capacity varies with temperature. Thus, the heat capacities at A and B are different.
- For gases, at a given temperature the slope of enthalpy versus temperature is **steeper than that** of internal energy versus temperature, and $C_{p,m}$ is **larger than** $C_{V,m}$

Heat Transaction and Enthalpy:

- By definition, $dH = dU + d(pV)$
- For an ideal gas, $pV = nRT$
$$\therefore dH = dU + R d(nT)$$
- For an ideal gas undergoing isothermal change in state (e.g. a gas phase chemical reaction at constant T),
$$dH = dU + RT d(n) \Rightarrow \Delta H = \Delta U + (\Delta n)RT$$
- For a non-reactive ideal gas undergoing heating/ cooling in a closed vessel
$$dH = dU + nR d(T) \Rightarrow \Delta H = \Delta U + nR \Delta T = (C_v + nR)\Delta T$$
$$\Delta H = C_p \Delta T$$

Heat Transactions

Therefore, in a **constant Pressure process**, the HEAT withdrawn from the surrounding (>0) is equal to the increase in the ENHALPY of the system



- for ideal/perfect gas; relation between ΔU and ΔH ,

$$H = U + PV (= nRT)$$

$$\Delta H = \Delta U + \Delta n_g RT$$

For an **ideal gas** undergoing **isothermal change in state** (e.g. a gas phase chemical reaction at constant T),

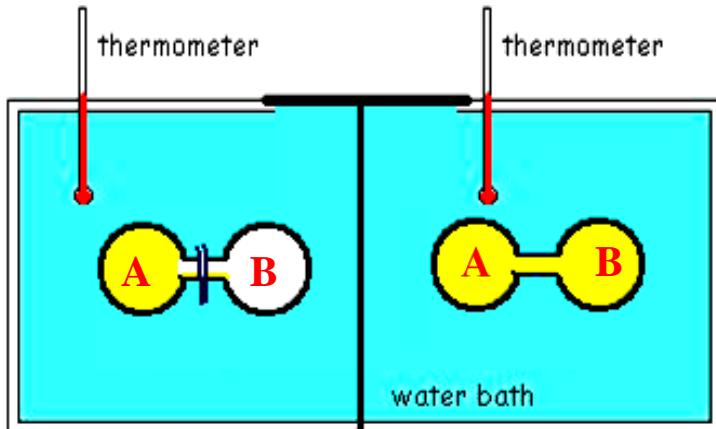
ΔH is the Enthalpy change occurring during reaction of gas molecules under constant T and P

Example: $2\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \longrightarrow 2\text{H}_2\text{O} (\text{l})$ here, $\Delta n = -3$ moles

$$\therefore \Delta H - \Delta U = -3RT$$

Joule's Experiment

Joule's Experiment



Flask A: Gas at high pressure (22 atm)

Flask B: High Vacuum

Both the flasks are connected by a valve, and the whole setup is kept in water bath and the bath temperature is monitored

$$dU_T = \left(\frac{\partial U}{\partial V} \right)_T dV = 0$$

$$\left(\frac{\partial U}{\partial P} \right)_T = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T = 0$$

$$\therefore \left(\frac{\partial U}{\partial P} \right)_T = 0$$

Observation:

No Temperature difference of the water before and after opening the stopcock.

1. $\delta_W = 0$ As expansion into vacuum

2. $\delta_q = 0$ As no heat entered or left as $\Delta T = 0$

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

Thus, $dU_T = 0$ within the accuracy of the expt.

$$\text{Now, } dU_T = \left(\frac{\partial U}{\partial V} \right)_T dV = 0$$

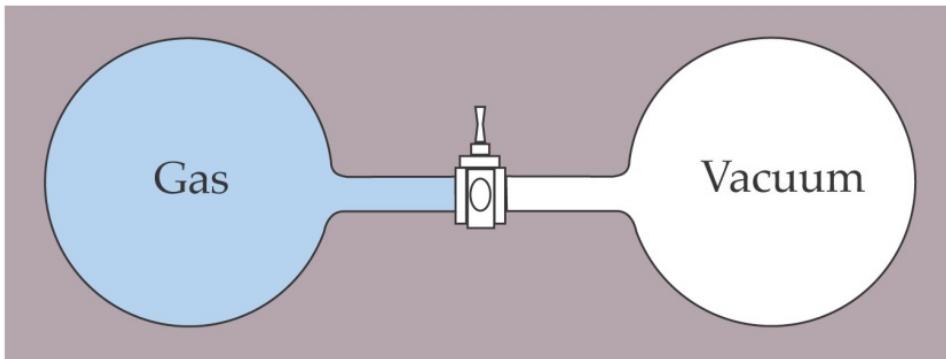
$$\because dV \neq 0 \quad \therefore \left(\frac{\partial U}{\partial V} \right)_T = 0$$

Thus, under the conditions mentioned, U is INDEPENDENT of V and $U = U(T)$ Joule's Law

Joule's Experiment

- Variation with volume at constant temperature

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



Joule's experiment

Isothermal expansion of an ideal gas against zero pressure

$$\delta w = 0$$
$$\delta q = 0$$

$$dU_T = \left(\frac{\partial U}{\partial V}\right)_T dV = 0$$

$$dV \neq 0 \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$$

for an ideal gas

In general,

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

Variation of **U** and **H** with the change in their **Fundamental Variables**

For any process

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

$$H = f(P, T)$$

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

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

$$= \pi_T dV + C_V dT$$

$$= \left(\frac{\partial H}{\partial P} \right)_T dP + C_P dT$$

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T \text{ Internal pressure}$$

$dU = C_V dT$ (for ideal gas)

For ideal gas

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = 0$$

Joule Experiment

$dH = C_p dT$ (for ideal gas)

For ideal gas

$$\left(\frac{\partial H}{\partial P} \right)_T = 0$$

Variation of U with the change in their Fundamental Variables

For any process

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

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

$$= \pi_T dV + C_V dT$$

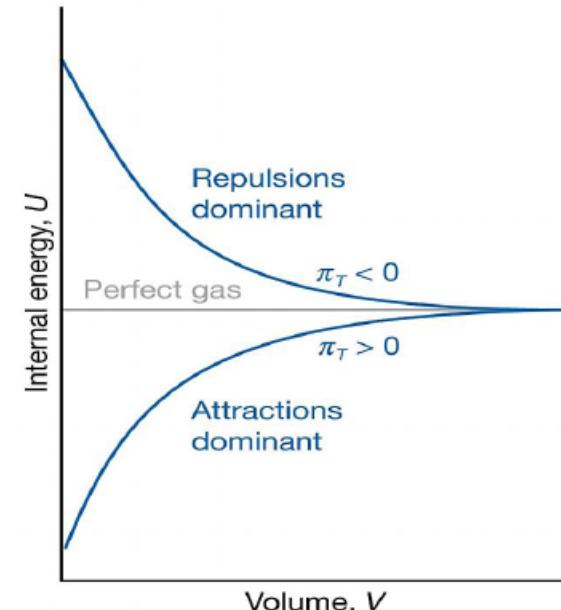
$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T \quad \text{Internal pressure}$$

$dU = C_V dT$ (for ideal gas)

For ideal gas

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = 0$$

Joule Experiment



- For ideal gas, $\pi_T = 0$ because U independent of molecular separation for volume changes at constant T

- For real gas,

If $dU > 0$ as dV increases with T constant, attractions between molecules dominate and $\pi_T > 0$

If $dU < 0$ as dV increases with T constant, repulsions between molecules dominate and $\pi_T < 0$

Heat Capacity

Transfer of heat to a system *may* result in a rise in T .

$$\delta q = C dT$$

↑ path function, so C depends on conditions.

Define: $\delta q_V = C_V dT$ at constant volume, *no work*

$\delta q_P = C_P dT$ at constant pressure, *only PV work*

From 1st Law, $dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV$ assume no other work
 $dU = \delta q_V$ for $dV = 0$

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

Similarly
$$\begin{aligned} dH &= dU + PdV + VdP \\ &= (\delta q - PdV) + PdV + VdP \\ &= \delta q_P \quad \text{for } dP = 0 \end{aligned}$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

For ideal gases $dH = dU + d(PV) = dU + nRdT$

$$C_P dT = C_V dT + nRdT$$

$$\bar{C}_P = \bar{C}_V + R$$



Appendix

The Relation Between C_P and C_V

$$\begin{aligned} C_P - C_V &= \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\ &= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \end{aligned}$$

$$H = U + PV$$

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

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Rightarrow C_P - C_V = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

work needed to
overcome intermolecular expansion per
 forces degree

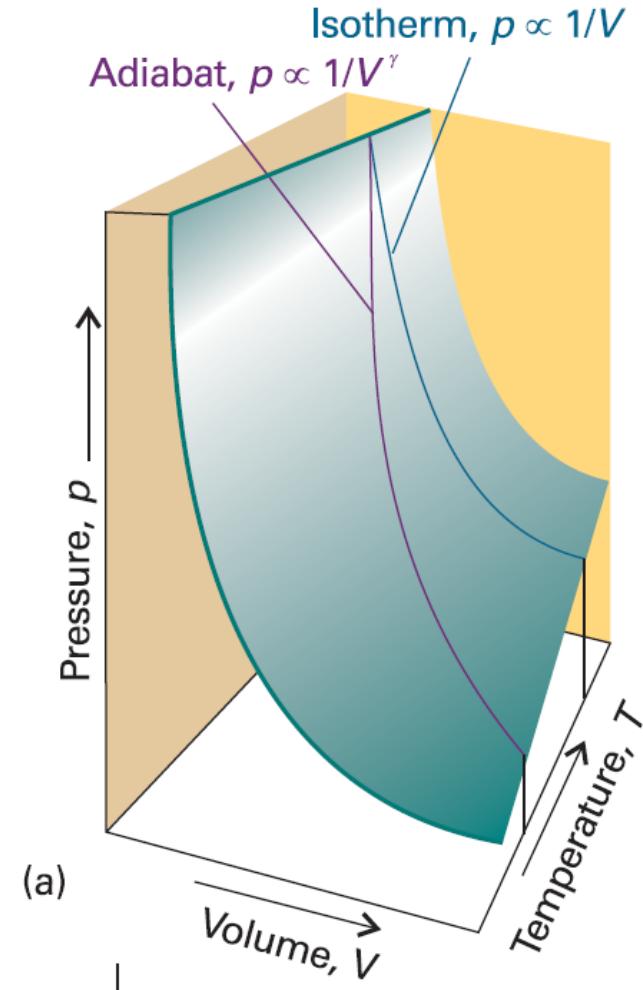
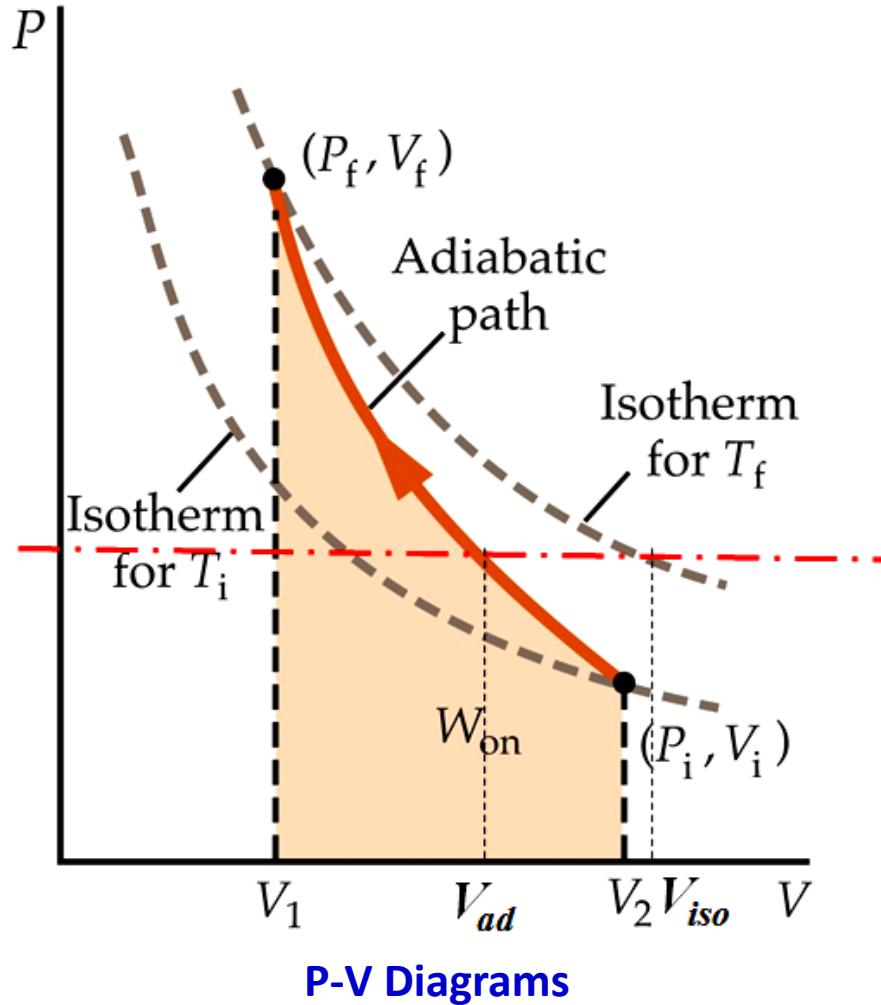
$\left(\frac{\partial U}{\partial V} \right)_T$ = “internal pressure”

For ideal
gases $\left(\frac{\partial U}{\partial V} \right)_T = 0, \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \Rightarrow C_P - C_V = nR$

For liquids
and solids $\left(\frac{\partial V}{\partial T} \right)_P$ is so small that $C_P \approx C_V$

Adiabatic Processes

No heat flows into or out of the system



Adiabatic Expansion 1

adiabatic = insulated:

$$\begin{array}{ll} q = 0, & \delta q = 0 \\ \Delta U = w & dU = \delta w \end{array}$$

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

$$\begin{aligned} w &= \int_1^2 dU = \int_{T_1}^{T_2} C_V dT + \dots \text{ (0 for ideal gases)} \\ &= C_V \Delta T \text{ if } C_V \text{ is independent of } T \end{aligned}$$

For adiabatic expansion $w \leq 0, \Delta U \leq 0 \Rightarrow T_2 \leq T_1$

Free expansion: $P_{\text{ex}} = 0 \Rightarrow w = 0, \Delta T = 0$

$$\begin{aligned} \text{Fixed pressure:} \quad w &= -P_{\text{ex}} \Delta V \\ w &= \Delta U = C_V \Delta T \\ \Rightarrow \Delta T &= -\frac{P_{\text{ex}} \Delta V}{C_V} \end{aligned}$$

Reversible expansion: $P = P_{\text{ex}}$

$$w = - \int_{V_1}^{V_2} P(V, T) dV$$

Substitute appropriate equation of state.

Not useful if T changes.

Adiabatic Expansion 1

Reversible adiabatic expansion of ideal gases:

$$dU = \delta w$$

$$\delta q = 0$$

$$C_V dT = -P dV = -\frac{nRT}{V} dV \quad \text{ideal gases only}$$

$$\bar{C}_V \int_1^2 \frac{1}{T} dT = -R \int_1^2 \frac{1}{V} dV$$

$$\begin{aligned}\bar{C}_V \ln(T_2/T_1) &= -R \ln(V_2/V_1) \\ &= -(\bar{C}_P - \bar{C}_V) \ln(V_2/V_1)\end{aligned}$$

$$\ln(T_2/T_1) = -(\gamma - 1) \ln(V_2/V_1)$$

$$\gamma = \frac{\bar{C}_P}{\bar{C}_V}$$

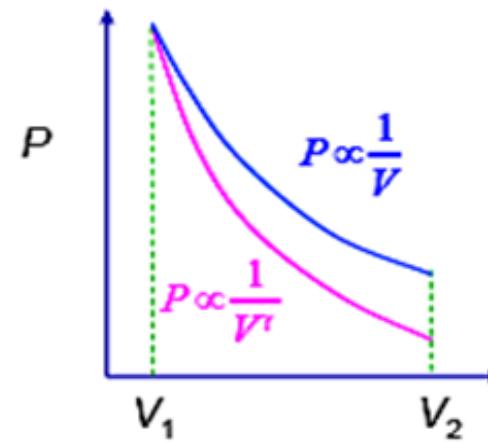
$$\boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}}$$

Also, since

$$\frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{\gamma} \quad \text{or} \quad P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(1-\gamma)/\gamma}}$$



Reversible Adiabatic Expansion and Compression

Adiabatic expansion

According to 1st Law

$$\Delta U = q + w$$

$$q=0$$

$$\Delta U = -w$$

$$\Delta U = n C_v \Delta T$$

$$-w = n C_v (T_f - T_i)$$

$$-w = n C_v (T_1 - T_2)$$

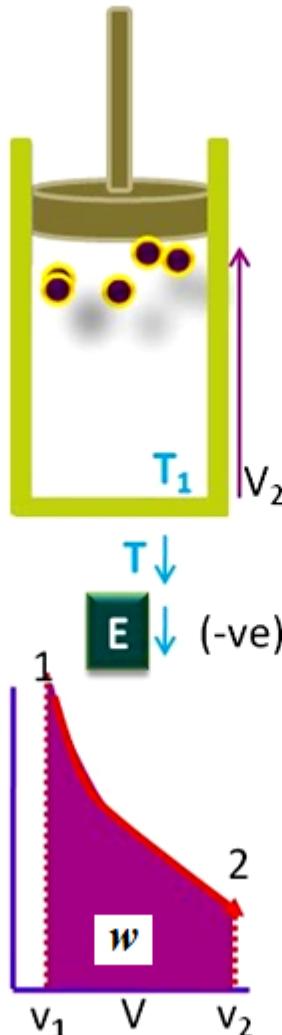
$$-w = -n C_v (T_2 - T_1)$$

$$\partial w = - \int \frac{nRT}{V} dV = -RT \ln\left(\frac{V_2}{V_1}\right)$$

$$nC_v dT = - \int \frac{nRT}{V} dV$$

For Monoatomic ideal gas:

$$C_V = \frac{3}{2}R ; C_p = \frac{5}{2}R \therefore \gamma = \frac{C_p}{C_V} = \frac{5}{3} (> 1)$$



Adiabatic compression

According to 1st Law

$$\Delta U = q + w$$

$$q=0$$

$$\Delta U = w$$

$$\Delta U = n C_v \Delta T$$

$$w = n C_v (T_f - T_i)$$

$$w = n C_v (T_2 - T_1)$$

$$TV^{\gamma-1} = \text{constant}$$

$$PV^\gamma = \text{constant}$$

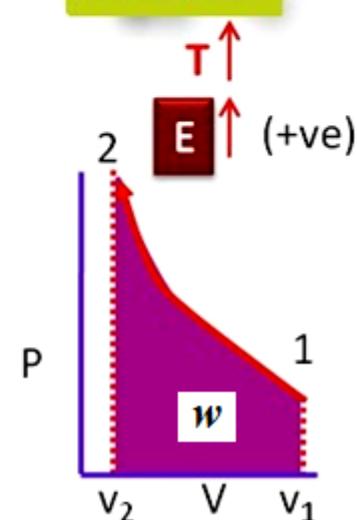
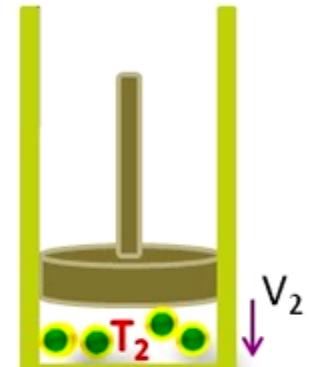
$$VT^c = \text{constant}$$

$$T^\gamma P^{1-\gamma} = \text{constant}$$

$$C_p - C_v = R$$

$$\text{where, } c = \frac{C_v}{R}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$



Reversible Adiabatic Process for Ideal Gas

1 mole gas (V_1, T_1) Rev. Adiabatic → 1 mole gas (V_2, T_2)

Adiabatic Process:

$$\partial q = 0$$

From 1st law:

$$dU = \partial q + \partial w \Rightarrow dU = \partial w$$

From Ideal gas:

$$dU = C_V dT \quad dU = nC_v dT$$

Work (Reversible) = $dw = -pdV$ (along the path) = $-\int pdV$

use: $p = \frac{nRT}{V}$

From 1st Law:

$$dU = \partial w$$

$$\Rightarrow nC_v dT = -\int \frac{nRT}{V} dV$$

$$\Rightarrow \bar{C}_v \int_{V_1}^{V_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow \bar{C}_v \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{V_1}{V_2}\right)$$

where, $\partial w = -\int \frac{nRT}{V} dV$

$$dU = nC_v dT$$

use: $\bar{C}_p - \bar{C}_v = R$

Define: $\gamma = \frac{C_p}{C_v} (> 1)$

$$\Rightarrow \left(\frac{T_2}{T_1}\right)^{C_v} = \left(\frac{V_1}{V_2}\right)^R \Rightarrow \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{R/C_v} \Rightarrow \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(C_p - C_v)/C_v} \Rightarrow \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

Reversible Adiabatic Process for Ideal Gas

Adiabatic Conditions for an Ideal Gas

$$TV^{\gamma-1} = \text{constant}$$

$$PV^\gamma = \text{constant}$$

$$VT^c = \text{constant}$$

$$\text{where, } c = \frac{C_V}{R}$$

$$T^\gamma P^{1-\gamma} = \text{constant}$$

Monoatomic: $C_V = \frac{3}{2}R \frac{J}{\text{mol} \cdot \text{K}}$

Diatomeric: $C_V = \frac{5}{2}R \frac{J}{\text{mol} \cdot \text{K}}$

Polyatomic: $C_V = \frac{6}{2}R \frac{J}{\text{mol} \cdot \text{K}}$

$$\text{Define: } \gamma = \frac{C_p}{C_V}$$

For Monoatomic ideal gas:

$$C_V = \frac{3}{2}R ; C_p = \frac{5}{2}R \therefore \gamma = \frac{C_p}{C_V} = \frac{5}{3} (> 1)$$

$$C_P = C_V + R \quad C_P - C_V = R$$

Reversible Adiabatic Expansion (or compression) of an Ideal Gas

In an adiabatic **EXPANSION** ($V_2 > V_1$); the gas cools down ($T_1 > T_2$)

In an adiabatic **COMPRESSION** ($V_2 < V_1$); the gas heats up ($T_2 > T_1$)

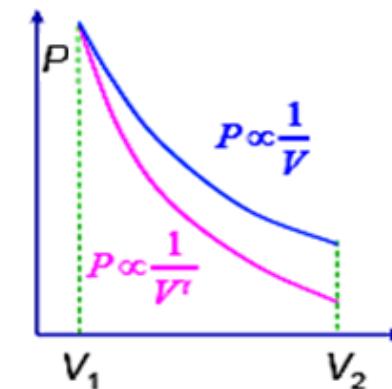
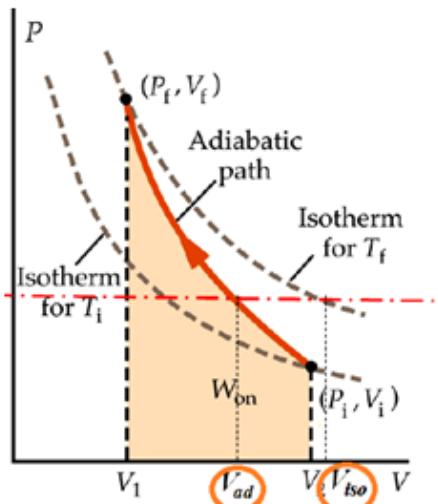
For an ideal gas (one mole):

$$T_1 = \frac{p_1 V_1}{R} \quad \text{and} \quad T_2 = \frac{p_2 V_2}{R}$$

$$\therefore \frac{T_1}{T_2} = \frac{p_1 V_1}{p_2 V_2}$$

$$\Rightarrow \left(\frac{p_1}{p_2} \right) = \left(\frac{V_2}{V_1} \right)^r \Rightarrow p_1 V_1^r = p_2 V_2^r$$

$pV^r = \text{constant}$ along a reversible adiabat



$V_{2, \text{adiabat}} > V_{1, \text{isothermal}}$

This is because the gas cools during Reversible Adiabatic Expansion

Adiabatic Irreversible Expansion of an ideal gas against a CONSTANT EXTERNAL PRESSURE

$$1 \text{ mol gas } (p_1, T_1) = 1 \text{ mol gas } (p_2, T_2) \quad (p_{\text{ext}} = p_2)$$

adiabatic $\Rightarrow dq = 0$

Constant $p_{\text{ext}} = p_2 \Rightarrow dw = -p_2 dV$

Ideal gas $\Rightarrow dU = C_V dT$

1st Law $\Rightarrow dU = -p_2 dV$

$$\therefore C_V dT = -p_2 dV$$

Integrating: $C_V (T_2 - T_1) = -p_2 (V_2 - V_1)$

Using $pV = RT$

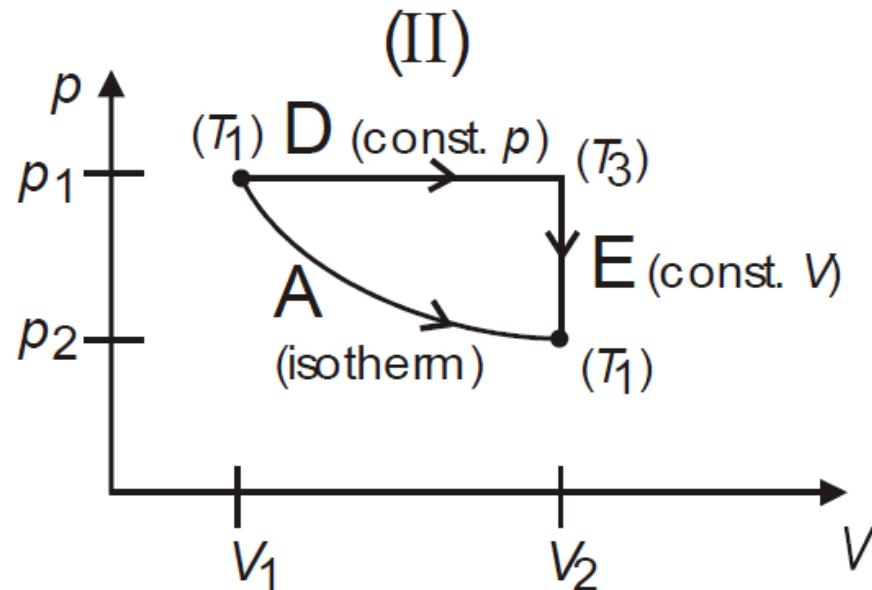
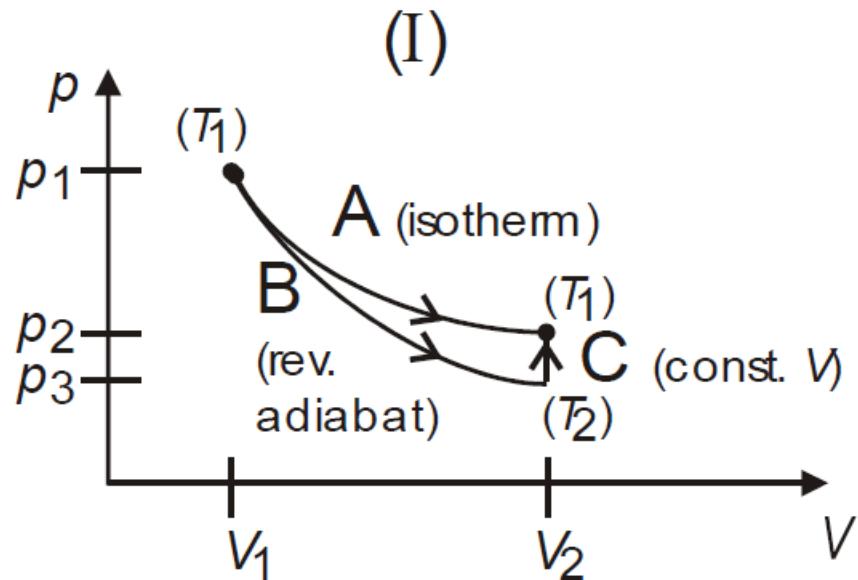
$$T_2(C_V + R) = T_1\left(C_V + \frac{p_2}{p_1}R\right)$$

Note $p_2 < p_1 \Rightarrow T_2 < T_1$ Again, expansion cools

Note also $(-W_{\text{rev}}) > (-W_{\text{irrev}})$ Less work is recovered through an irreversible process

Numerical Problems on some Thermodynamic Cycles

For the Reversible Ideal Gas processes: Find $\Delta U, \Delta H, q, w, dq/T$



Path [A]: 1 mol gas $(p_1, V_1, T_1) \xrightarrow{\text{const. } T} 1 \text{ mol gas } (p_2, V_2, T_1)$

Ideal gas isotherm: $\boxed{\Delta U_A = 0}$ $\boxed{\Delta H_A = 0}$

$$w_A = -RT_1 \ln \frac{V_2}{V_1} ; \quad q_A = RT_1 \ln \frac{V_2}{V_1} ; \quad \int \frac{dq}{T} = R \ln \frac{V_2}{V_1}$$

Numerical Problems on some Thermodynamic Cycles

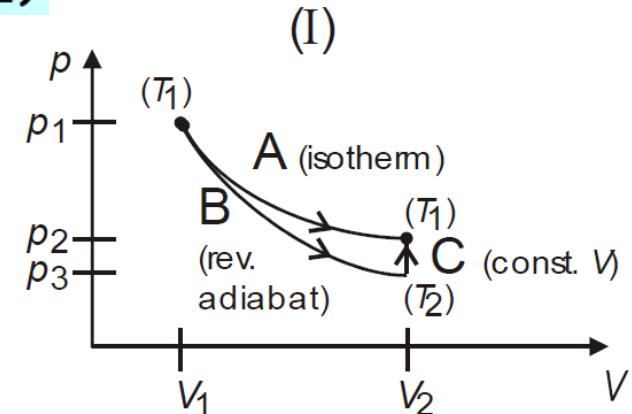
Path [B]:

$$1 \text{ mol gas } (p_1, V_1, T_1) \xrightarrow{\text{rev. adiabat}} 1 \text{ mol gas } (p_3, V_3, T_2)$$

Adiabat: $q_B = 0$

Ideal gas: $\Delta U_B = C_V (T_2 - T_1)$; $\Delta H_B = C_p (T_2 - T_1)$

1st Law: $w_B = C_V (T_2 - T_1)$; $\int \frac{dq_B}{T} = 0$



Path [C]:

$$1 \text{ mol gas } (p_3, V_2, T_2) \xrightarrow[\text{const. } V]{\text{reversible}} 1 \text{ mol gas } (p_2, V_2, T_1)$$

Constant V: $w_C = 0$; 1st Law: $q_C = C_V (T_1 - T_2)$

Ideal gas: $\Delta U_C = C_V (T_1 - T_2)$; $\Delta H_C = C_p (T_1 - T_2)$; $\int \frac{dq_C}{T} = C_V \ln \left(\frac{T_1}{T_2} \right)$

Numerical Problems on some Thermodynamic Cycles

Now, compare path [A] **verses** path [B] + [C]

Path

[A]

Path

[B] + [C]

$$\Delta U_A = 0$$

$$\Delta H_A = 0$$

$$\Delta U_B + \Delta U_C = 0 = \Delta U_A$$

$$\Delta H_B + \Delta H_C = 0 = \Delta H_A$$

$$q_A = RT_1 \ln \frac{V_2}{V_1}$$

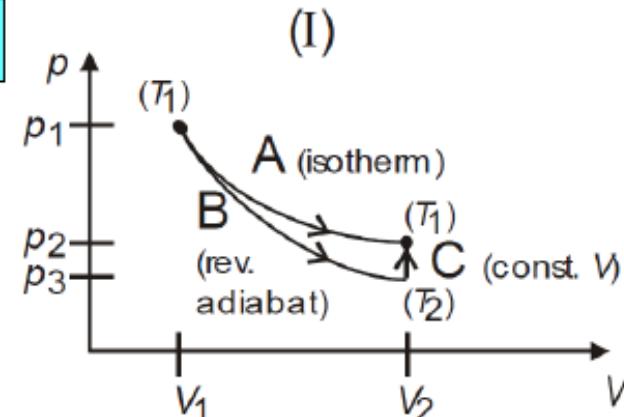
$$w_A = -RT_1 \ln \frac{V_2}{V_1}$$

$$\int \frac{dq_A}{T} = R \ln \frac{V_2}{V_1}$$

$$q_B + q_C = C_V (T_1 - T_2) \neq q_A$$

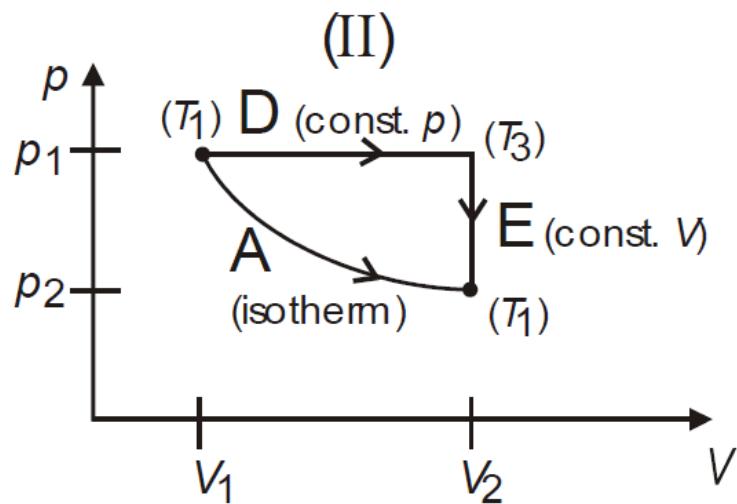
$$w_B + w_C = C_V (T_2 - T_1) \neq w_A$$

$$\int \frac{dq_B}{T} + \int \frac{dq_C}{T} = R \ln \left(\frac{V_2}{V_1} \right) = \int \frac{dq_A}{T}$$



- Here we see from the calculation that the change state of an ideal gas, operating through path [A] and [B] + [C], have the same value of $\int dq/T$.
- Therefore, $\int dq/T$ seems **INDEPENDENT** of the PATH followed for the process and depends only on the initial and final state. And hence it is a **STATE** functions

Numerical Problems on some Thermodynamic Cycles



Path [D]:

$$\begin{aligned}\Delta U_D &= C_V (T_3 - T_1) \\ \Delta H_D &= C_p (T_3 - T_1)\end{aligned};$$

$$q_D = C_p (T_3 - T_1);$$

$$w_D = -R(T_3 - T_1);$$

$$\int \frac{dq_D}{T} = C_p \ln\left(\frac{T_3}{T_1}\right)$$

Path [E]:

$$\Delta U_E = C_V (T_1 - T_3)$$

$$\Delta H_E = C_p (T_1 - T_3)$$

$$w_E = 0;$$

$$q_E = C_V (T_1 - T_3)$$

$$\int \frac{dq_E}{T} = C_V \ln\left(\frac{T_1}{T_3}\right)$$

Numerical Problems on some Thermodynamic Cycles

Now, compare path [A] **verses** path [D] + [E]

Path [A]:

$$\Delta U_A = 0$$

$$\Delta H_A = 0$$

$$q_A = R T_1 \ln \frac{V_2}{V_1}$$

$$w_A = -R T_1 \ln \frac{V_2}{V_1}$$

$$\int \frac{dq_A}{T} = R \ln \frac{V_2}{V_1}$$

Path [D] + [E]:

$$\Delta U_D + \Delta U_E = \Delta U_A$$

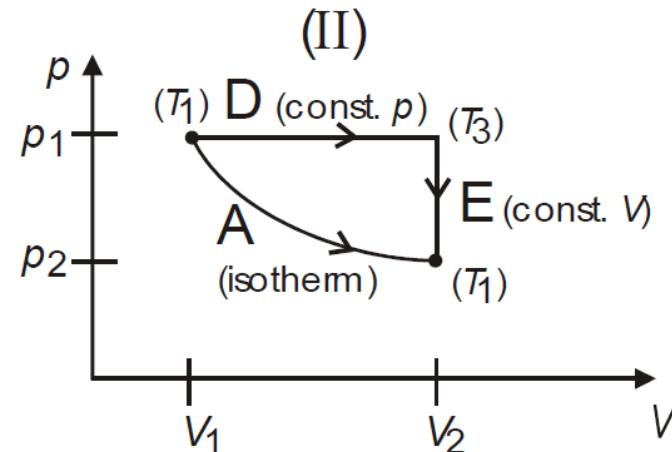
$$\Delta H_D + \Delta H_E = \Delta H_A$$

$$q_D + q_E = R(T_3 - T_1) \neq q_A$$

$$w_D + w_E = -R(T_3 - T_1) \neq w_A$$

$$\int \frac{dq_D}{T} + \int \frac{dq_E}{T} = R \ln \left(\frac{V_2}{V_1} \right) = \int \frac{dq_A}{T}$$

Here again $\left(\int \frac{dq_{rev}}{T} \right)$ looks like a state function!



We will discuss this term later while dealing with 2nd Law of Thermodynamics

Numerical Problems on some Thermodynamic Cycles

Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 cm³. at 298.15 K to 2.00 dm³.

For reversible adiabatic expansion

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c} \quad [2.28a]$$

where

$$c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = \frac{(37.11 - 8.3145) \text{ J K}^{-1}\text{mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1}} = 3.463,$$

so the final temperature is

$$T_f = (298.15 \text{ K}) \times \left(\frac{500 \times 10^{-3} \text{ dm}^3}{2.00 \text{ dm}^3} \right)^{1/3.463} = \boxed{200 \text{ K}}$$

A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from 400 cm³ to 2.00 dm³. What is the work done by the gas?

Reversible adiabatic work is

$$w = C_V \Delta T \quad [2.27] = n(C_{p,m} - R) \times (T_f - T_i)$$

where the temperatures are related by $T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$

$$\text{where } c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = 2.503$$

Numerical Problems on some Thermodynamic Cycles

$$\text{So } T_f = [(23.0 + 273.15) \text{ K}] \times \left(\frac{400 \times 10^{-3} \text{ dm}^3}{2.00 \text{ dm}^3} \right)^{1/2.503} = 156 \text{ K}$$

$$\text{and } w = \left(\frac{3.12 \text{ g}}{28.0 \text{ g mol}^{-1}} \right) \times (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1} \times (156 - 296) \text{ K} = \boxed{-325 \text{ J}}$$

Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 cm³ to a final volume of 3.0 dm³. Take $\gamma = 1.3$

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{so} \quad p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma = (8.73 \text{ Torr}) \times \left(\frac{500 \times 10^{-3} \text{ dm}^3}{3.0 \text{ dm}^3} \right)^{1.3} = \boxed{8.5 \text{ Torr}}$$

VARIATION OF $\textcolor{red}{U}$ with SYSTEM VARIABLES:

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

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

1. Change in $\textcolor{blue}{U}$ w.r.t. T at **constant volume**

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V ; q_v = C_v \Delta T = \Delta U$$

2. Change in $\textcolor{blue}{U}$ w.r.t. V at **constant temp:**

$$dU = \pi_r dV + C_v dT \quad \text{For real gas}$$

$$dU = C_v dT \quad (\text{for ideal gas}) \quad \text{As For ideal gas}$$

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

$$\pi_r = \left(\frac{\partial U}{\partial V} \right)_T = 0$$

3. Change in $\textcolor{blue}{U}$ w.r.t. T at **constant pressure**

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

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

$$\left(\frac{\partial U}{\partial T} \right)_P = C_v + \alpha V \left(\frac{\partial U}{\partial V} \right)_T$$

where

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

Variation of Internal Energy U with System Properties

- Variation with temperature at constant pressure

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

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

Let us define the isobaric expansion coefficient

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

Thus,

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

Change in Internal Energy, U at Constant P

- Suppose we want to know how the internal energy, U , changes with temperature at constant pressure

$$dU = \pi_T dV + C_v dT$$

$$\left(\frac{\partial U}{\partial T} \right)_p = \left(\frac{\partial (\pi_T dV + C_v dT)}{\partial T} \right)_p$$

$$\left(\frac{\partial U}{\partial T} \right)_p = \pi_T \left(\frac{\partial V}{\partial T} \right)_p + C_v$$

- But the change in volume with temperature at constant pressure is related to the Isobaric thermal expansion / expansion coefficient of the gas, α

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

$$\text{so} \quad \left(\frac{\partial U}{\partial T} \right)_p = \pi_T \alpha V + C_v$$

- Large α means sample responds strongly to changes in T
- For an ideal gas, $\pi_T = 0$ so

$$\left(\frac{\partial U}{\partial T} \right)_p = C_v \quad (\text{definition})$$

Variation of V with System Variables:

Experimentally known that the Volume of an isotropic material is a function of Temperature and Pressure

$$V = V(T, p)$$

$$dV = \left(\frac{\partial V}{\partial p} \right)_T dp + \left(\frac{\partial V}{\partial T} \right)_p dT.$$

$$\frac{dV}{V} = \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T dp + \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p dT.$$

$$\frac{dV}{V} = -\kappa_T dp + \alpha dT,$$

relative/fractional change of Volume

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

isothermal compressibility

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

Isobaric thermal expansion / expansion coefficient

For an ideal gas : $PV = nRT$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \text{Similarly, } \kappa_T = 1/p$$

$$= \frac{1}{V} \left(\frac{nR}{p} \right) = \frac{nR}{pV}$$

For solid and liquid, α and κ_T are approximately independent of T & p

$$= \frac{1}{T}.$$

Variation of P with System Variables:

Another quantity of interest which can be obtained from α and κ_T is:

This derivative tells us how fast the pressure rises when we try to keep the volume constant while increasing the temp.

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

Exercise:

How much pressure would be generated in a mercury thermometer if we tried to heat the thermometer higher than the temperature where the mercury has reached the top of the thermometer. Given: For Hg, $\alpha = 1.82 \times 10^{-4} \text{ K}^{-1}$ and $\kappa_T = 3.87 \times 10^{-5} \text{ atm}^{-1}$

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa_T}.$$

$$= \frac{1.82 \times 10^{-4} \text{ K}^{-1}}{3.87 \times 10^{-5} \text{ atm}^{-1}} dT$$

$$= 4.70 \text{ atm/K} dT.$$

We see that each 1 C increases the pressure by 4.7 atm, about 69 lb/sq in. This is a lot of pressure for a glass tube to withstand. It wouldn't take very many degrees of temperature increase to break the glass thermometer!!!

Using a variation of Euler's chain rule we can write

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

$$\begin{aligned} \left(\frac{\partial p}{\partial T} \right)_V &= - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} &= - \frac{\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p}{\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T} &= \frac{\alpha}{\kappa_T}. \end{aligned}$$

Variation of H with System Variables:

$$H = f(P, T)$$

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

1. Change in H w.r.t. T at Constant Pressure

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P ; q_p = C_p \Delta T = \Delta H$$

2. Change in H w.r.t. P at Constant Temperature:

$$H = f(P, T)$$

Apply Euler's chain rule

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

$$\therefore \left(\frac{\partial H}{\partial P} \right)_T = - \left(\frac{\partial T}{\partial P} \right)_H \left(\frac{\partial H}{\partial T} \right)_P = -\mu_{JT} C_p$$

Joule-Thomson coefficient (μ_{JT})

$$\left(\frac{\partial H}{\partial P} \right)_T$$

For Ideal Gas:

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + C_p dT$$

$$dH = C_p dT \text{ (For Ideal Gas)}$$

For ideal gas $\left(\frac{\partial H}{\partial P} \right)_T = 0$

Variation of H with System Variables:

3. Change in H w.r.t. T at constant volume:

$$\left(\frac{\partial H}{\partial T} \right)_V$$

$$dH = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

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

From earlier results

$$\left(\frac{\partial H}{\partial P} \right)_T = -\mu_{JT} C_p ; \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\kappa_T}$$

$$\therefore \left(\frac{\partial H}{\partial T} \right)_V = C_p \left[1 - \frac{\alpha \mu_{JT}}{\kappa} \right]$$

where,

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

Isobaric expansion coefficient

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Isothermal compressibility

The Joule-Thomson Expansion Expt

For Ideal Gas:

$$\left(\frac{\partial H}{\partial P} \right)_T = 0$$

But for Real Gas:

$$\left(\frac{\partial H}{\partial P} \right)_T = -C_p \mu_{JT} \neq 0$$

The Joule-Thomson experiment consists of forcing a gas at constant backing pressure passing through a porous plug under adiabatic condition and measuring the change in temperature.

The Joule-Thomson coefficient (μ_{JT}) =

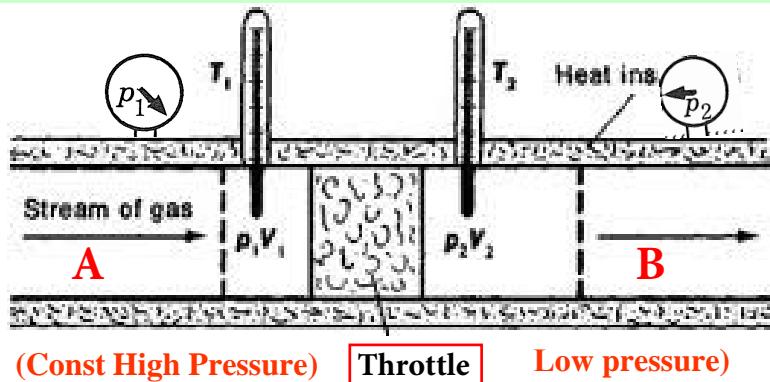
$$\left(\frac{\partial T}{\partial p} \right)_H \approx \left(\frac{\Delta T}{\Delta p} \right)$$

The most straightforward way to measure the coefficient is to measure the temperature of the gas entering and leaving the porous plug and divide the change in temperature by the change in pressure:

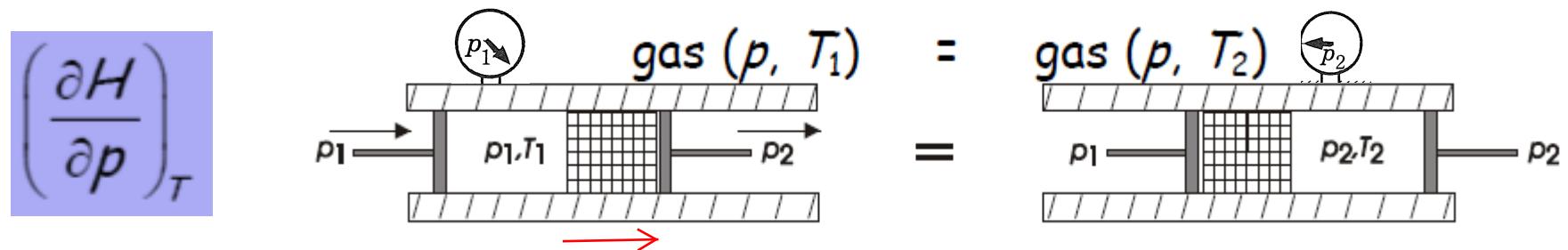
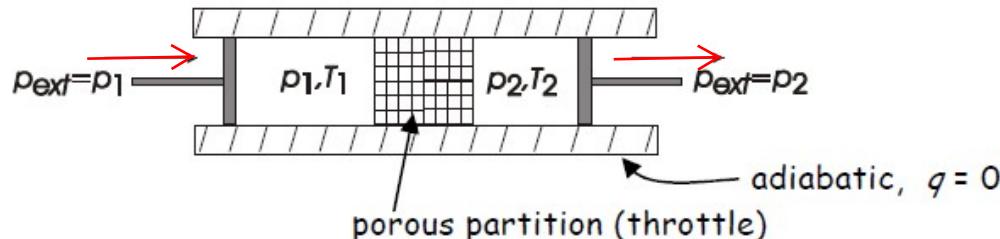
$$\left(\frac{\partial T}{\partial P} \right) \approx \frac{\Delta T}{\Delta P} = \frac{T_2 - T_1}{P_2 - P_1}$$

we need to decide what is being held constant when we take the partial derivative. In this case, since $q=0$, the change in internal energy of the gas is equal to w .

The Joule-Thomson Expansion Expt



\Rightarrow Joule-Thomson expansion



In this experiment $q = 0$; $w = [- p_2 (V_2 - 0)] + [- p_1 (0 - V_1)]$

$$\Delta U = U_2 - U_1 = q + w = - p_2 V_2 + p_1 V_1$$

$$U_2 + p_2 V_2 = U_1 + p_1 V_1 \quad H_f = H_i$$

$$\therefore \boxed{\Delta H = 0}$$

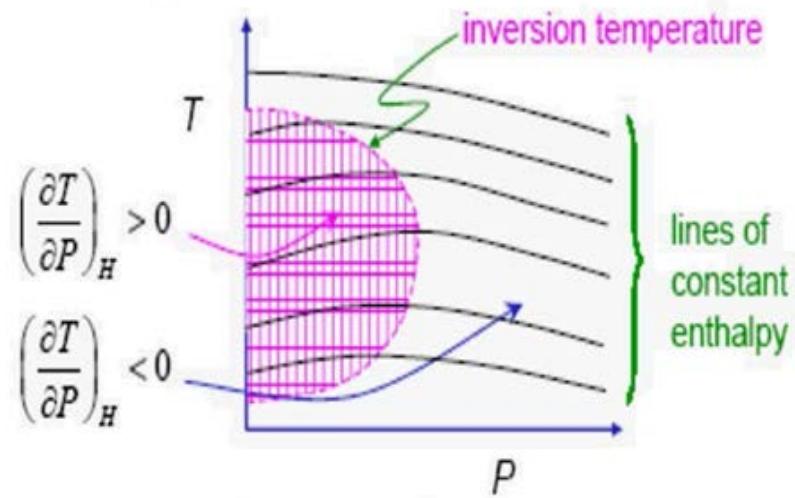
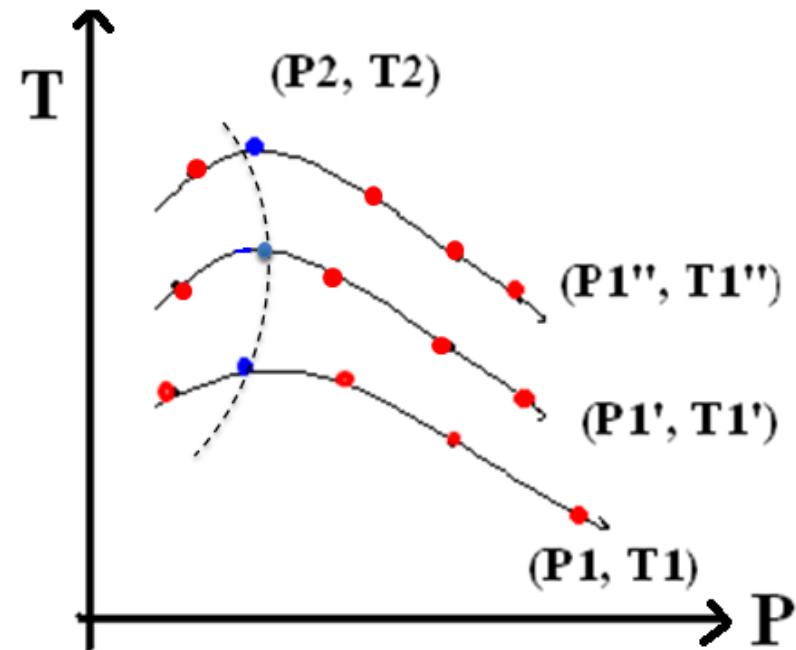
Isenthalpic process

- The gas in A is compressed Isothermally under const Pressure p_1 so that its volume changes from V_1 to 0. After crossing the porous plug, the gas in B expands from 0 to V_2 .
- Boundary of the system moves with the gas so as to enclose the same mass of gas

THE JOULE-THOMPSON EXPERIMENT

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

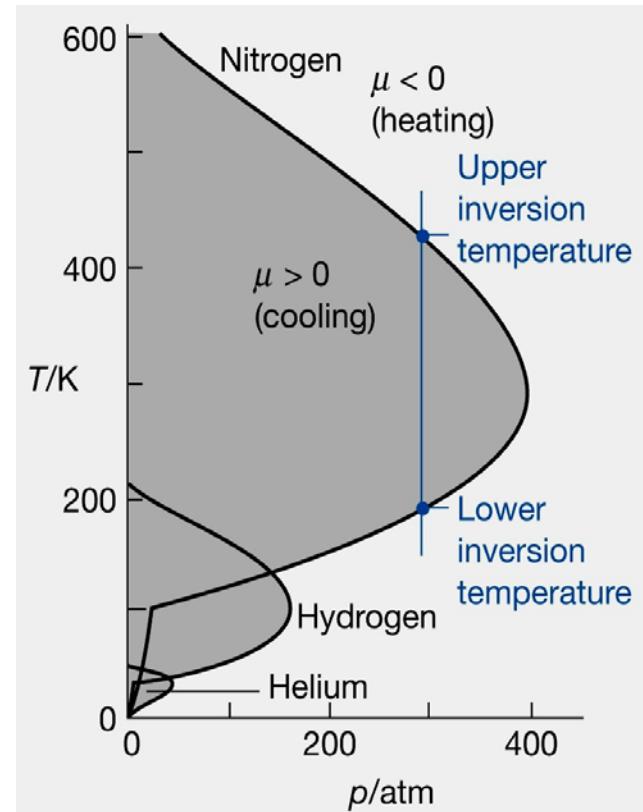
- If $\mu > 0$ then this indicates that the gas cools ($-ve \delta T$) when gas expanded ($-ve \delta p$).
- If $\mu < 0$ then this indicates that the gas heats ($+ve \delta T$) when expanded ($-ve \delta p$).
- The "inversion temperature" indicates where on a (T, p) isenthalpic plot the $(dT/dP)_H$ flips from $+ve$ to $-ve$. Or, point where μ changes sign from $+$ to $-ve$ and the point is the maximum inversion temperature
- For a real gas μ is non-zero (except at the maximum inversion temperature)



THE JOULE-THOMPSON EXPERIMENT

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

- μ can be either (+) or (-)
 - Positive μ means dT is negative when dp is negative
 - Gas cools on expansion
 - Negative μ means that means dT is positive when dp is negative
 - Gas warms on expansion
 - Transition between positive and negative μ is called the Joule-Thompson inversion temperature
 - Gases have both high and low inversion temperatures
 - Ideal gas $\mu = 0$, T unchanged by change in p on expansion
- Practical applications:
 - Gas liquefaction
 - Isotope separation



Gas	T _{inversion} (K)	μ (K atm ⁻¹)
C ₂ O	1 5 0 0	1.1 1
N ₂	6 2 1	0.2 5
He	6 2 1	0.2 5

THE JOULE-THOMPSON EXPERIMENT

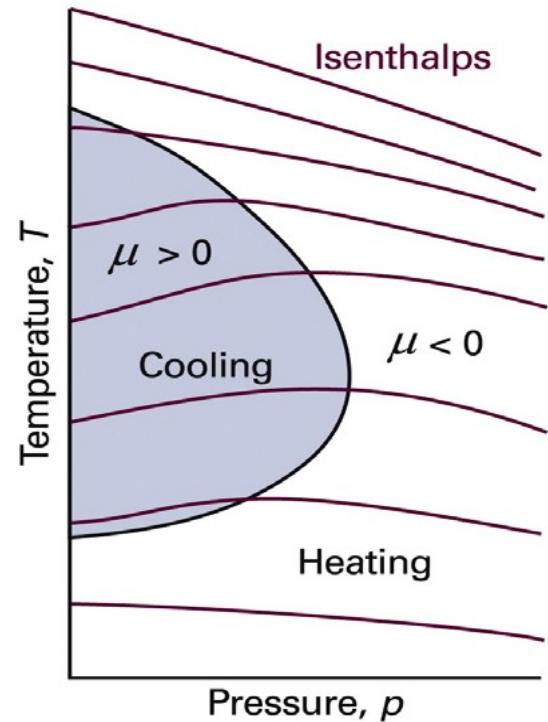
Joule-Thomson Expansion

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

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

m_{JT} is positive then dT is negative upon expansion so that the gas cools.

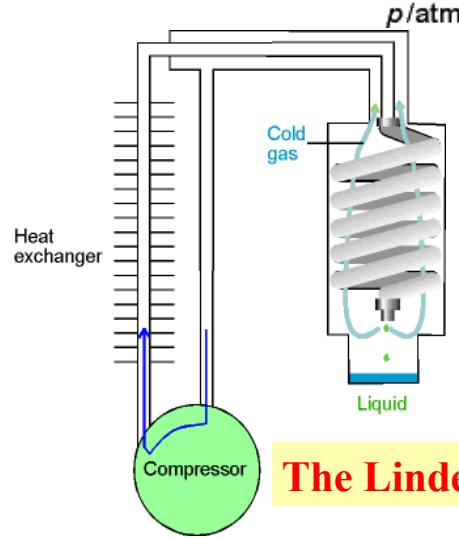
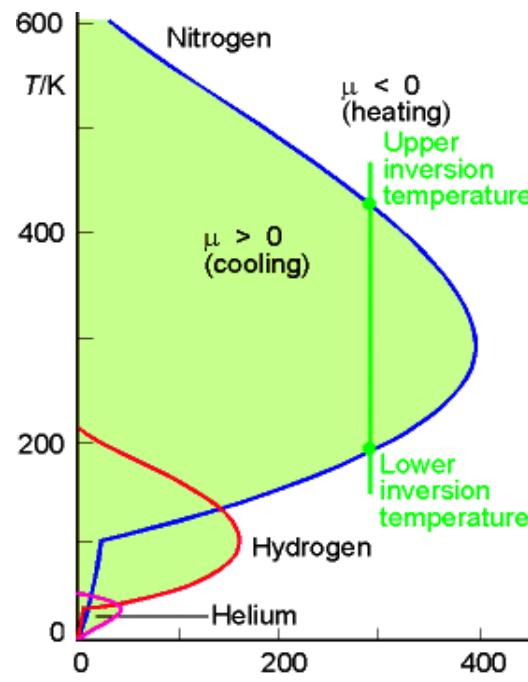
In order to liquefy a gas by a Joule-Thomson expansion the gas must first be cooled to below the J-T inversion temperature.



He	40 K
H ₂	202 K
Ne	231 K
—	—
N ₂	621 K
Air	673 K
O ₂	764 K
CO ₂	1500K

N₂ and O₂ will cool upon expansion at room temperature, but He, H₂ and Ne will warm upon expansion at room temperature.

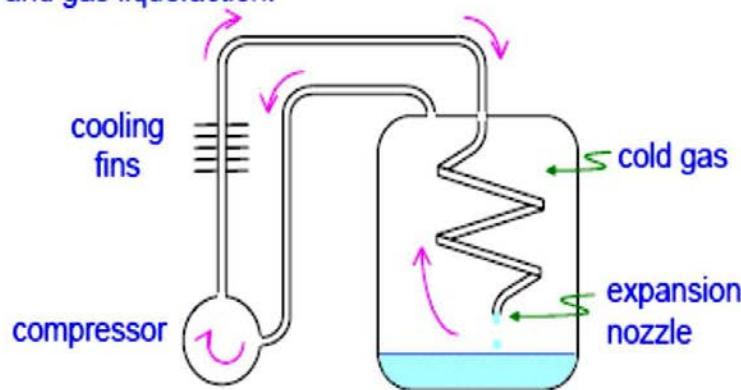
THE JOULE-THOMPSON EXPERIMENT



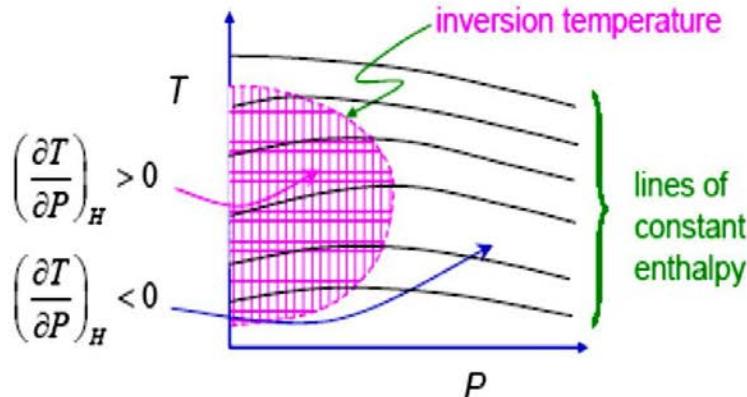
The Linde process

The Linde Refrigerator

For most gases at room temperature $\mu_{JT} > 0$ so sudden (adiabatic) expansion results in a drop in T. This is the basis of operation of the **Linde refrigerator** and gas liquefaction.



In general, μ_{JT} depends on T and can even change sign.



Joule Thomson Coefficient for a van der Waal Gas:

$$P = \frac{RT}{(\bar{V} - b)} - \frac{a}{\bar{V}^2}$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T \left(\frac{\partial V}{\partial T} \right)_p - V}{C_p}$$

$$p = \frac{RT}{\bar{V}} \left[\frac{1}{1 - \frac{b}{\bar{V}}} - \frac{a}{RT\bar{V}} \right]$$

From calculus:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots$$

$$p = \frac{RT}{\bar{V}} \left[1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \dots - \frac{a}{RT\bar{V}} \right] = \frac{RT}{\bar{V}} \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{\bar{V}} + \left(b^2 \right) \frac{1}{\bar{V}^2} + \dots \right]$$

$$Z = \frac{p\bar{V}}{RT}$$

$$B = b - \frac{a}{RT}$$

B
second virial
coefficient

C
third virial
coefficient

$$C = b^2$$

$$Z = 1 + \left(b - \frac{a}{RT} \right) \frac{p}{RT} + \dots$$

Joule Thomson Coefficient for a van der Waal Gas:

The Joule-Thomson coefficient

$$p = \frac{RT}{V} \left[1 + \frac{b}{V} + \frac{b^2}{V^2} + \dots - \frac{a}{RTV} \right] = \frac{RT}{V} \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{V} \right]$$

$$\bar{V} = \frac{RT}{p} \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{V} \right] \rightarrow \bar{V} = \frac{RT}{p} + b - \frac{a}{RT} + \dots$$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p} + \frac{a}{RT^2} + \dots$$

$$T \left(\frac{\partial V}{\partial T} \right)_p = \frac{RT}{p} + \frac{a}{RT} + \dots$$

$$T \left(\frac{\partial V}{\partial T} \right)_p - \bar{V} = \frac{RT}{p} + \frac{a}{RT} - \frac{RT}{p} + \frac{a}{RT} - b = \frac{2a}{RT} - b + \dots$$

$$\mu_{JT} = \frac{\frac{2a}{RT} - b}{C_p} + \dots$$

Very low T

$$\mu_{JT} = \frac{2a}{RTC_p}$$

A Positive JT coefficient means **cooling**

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T \left(\frac{\partial V}{\partial T} \right)_p - V}{C_p}$$

↓ Applied to van der Waal Gas

$$\mu_{JT} = \frac{\left(\frac{2a}{RT} - b \right)}{C_p} + \dots$$

Look at the extremes

Very high T

$$\mu_{JT} = - \frac{b}{C_p}$$

A Negative JT coefficient means **heating**

- If the initial temperature is above the inversion temperature, the final temperature is *higher* than the initial T (**heating occurs**)
- If initial temperature is below the inversion temperature, the final temperature is *lower* than the initial T (**cooling occurs**)

Joule Thomson Coefficient for a van der Waal Gas:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T \left(\frac{\partial V}{\partial T} \right)_p - V}{C_p}$$

Applied to van der Waal Gas

$$\mu_{JT} = \left(\frac{2a}{RT} - b \right) + \dots \Leftrightarrow \mu_{JT} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right)$$

Inversion Temperature

$$\mu_{JT} = \left(\frac{2a}{RT} - b \right) ;$$

At Inversion Temperature, T_{inv} , $\mu_{JT} = 0$

\therefore To find T_{inv} , put $\mu_{JT} = 0$

$$\text{So, } \left(\frac{2a}{RT_{inv}} - b \right) = 0 \Leftrightarrow \frac{2a}{RT_{inv}} = b$$

If $\left(\frac{2a}{RT} > b \right)$ then $\mu_{JT} > 0$ [COOLING OBSERVED]

If $\left(\frac{2a}{RT} < b \right)$ then $\mu_{JT} < 0$ [HEATING OBSERVED]

$$T_{inv} = \frac{2a}{Rb}$$

- Therefore, μ_{JT} depends critically on the constants a and b , which are the indices of non zero interaction and finite volume of the gas molecules respectively

- If initial Temp (T_1) is below $T_{inversion}$ only then cooling is observed and the final temp T_2 is lower than T_1

Derive the Following Expressions

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

$$C_p - C_V = \frac{\alpha^2 TV}{\kappa}$$

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

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

For ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial U}{\partial p}\right)_T = 0$$

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

$$\left(\frac{\partial H}{\partial V}\right)_T = 0$$

- $\mu_{JT} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T$
- $\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{T (\partial V / \partial T)_p - V}{C_p}$
- **For Ideal Gas:** $\mu_{JT} = 0$
- **For Real Gas:** $\mu_{JT} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right)$

Isothermal Joule-Thomson Coefficient, $\mu_T = \left(\frac{\partial H}{\partial p}\right)_T$

$$\therefore \mu_T = -C_p \times \mu_{JT}$$

Monoatomic ideal gas $C_{V,m} = 3R/2$, $C_{p,m} = 5R/2$

Various Forms of C_p and C_v Relationships

Derive:

$$C_p - C_v = p \left(\frac{\partial V}{\partial T} \right)_p + \alpha \pi_T V$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \text{ and } C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad [\text{definition}]$$

$$\text{and } H = U + pV \quad [\text{definition}]$$

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

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

$$\text{or, } C_p - C_v = \left(\frac{\partial pV}{\partial T} \right)_p + \left(\frac{\partial U}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v$$

But we saw: $\left(\frac{\partial U}{\partial T} \right)_p = \alpha \pi_T V + C_v$

$$\text{and } \left(\frac{\partial U}{\partial T} \right)_v = C_v$$

$$\text{so, } C_p - C_v = \left(\frac{\partial pV}{\partial T} \right)_p + \alpha \pi_T V + C_v - C_v$$

$$C_p - C_v = p \left(\frac{\partial V}{\partial T} \right)_p + \alpha \pi_T V$$

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

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

$$\left(\frac{\partial U}{\partial T} \right)_p = \pi_T \left(\frac{\partial V}{\partial T} \right)_p + C_v = \pi_T \alpha V + C_v$$

Various Forms of C_p and C_v Relationships

Derive:

$$C_p - C_v = \frac{\alpha^2 VT}{\kappa_T}$$

$$C_p - C_v = p \left(\frac{\partial V}{\partial T} \right)_p + \alpha \pi_T V$$

$$\Rightarrow C_p - C_v = p\alpha V + \alpha \pi_T V = \alpha V(p + \pi_T)$$

Putting, $\pi_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$

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

$$\Rightarrow C_p - C_v = \alpha V \left[T \left(\frac{\partial p}{\partial T} \right)_V \right]$$

From Isothermal Expansion Coefficient, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

$$\Rightarrow C_p - C_v = \alpha V T \left(\frac{\alpha}{\kappa_T} \right)$$

Putting, $\left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa_T}$

$$C_p - C_v = \frac{\alpha^2 VT}{\kappa_T}$$

- For an Ideal Gas, this reduces to what we found earlier

$$\begin{aligned} \alpha & (\text{Isothermal Expansion Coeff.}) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{T} \\ \kappa_T & (\text{Isobaric Expansion Coeff.}) = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{P} \end{aligned} \quad] \quad \text{this reduces to} \quad C_p - C_v = R$$

Conclusion of Ist Law of Thermodynamics

- The internal energy of an isolated system is a constant
For isolated system : $dU = 0$; (as $q = 0$, $w = 0 \gg$ No perpetual motion machines!)
- The energy of the universe is constant. $\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}}$
- When a system undergoes a process that leads to a change of state then the sum of the heat **q** transferred and the work **w** performed, is equal to the change in the internal energy **dU** of the system.
 $dU = \partial q + \partial w$ (**Closed system, through a number of steps**)
- A system contains ONLY internal energy. A system does not contain heat or work.

Conclusion of Ist Law of Thermodynamics

- Cyclic Process $\rightarrow \oint dU = 0$ (Exact differential)
- In a cyclic process the work done by a system on its surroundings is equal to the heat withdrawn from the surroundings. $\rightarrow -\delta w = \delta q$
- For an Adiabatic Process $\rightarrow \delta w_{ad} = dU$; (as $\delta q = 0$)
- For a Non-Adiabatic Process $\rightarrow \delta q = dU - \delta w \equiv \delta q = (\delta w_{ad} - \delta w)$; (as, $\delta w_{ad} = dU$)

Appendix

Calculation of thermodynamic functions for various processes

	reversible phase change at const. T, p	const p heating, no phase change	const V heating, no phase change
w	$- \int p dV = -p\Delta V$	$- \int p dV = -p\Delta V$	0
q	latent heat	$q_p = \Delta H$	$q_V = \Delta U$
ΔU	$q + w$	$q + w$	$= \int C_V(T) dT$
ΔH	q	$= \int C_p(T) dT$	$\Delta U + V\Delta p$

Calculation of thermodynamic function for various processes for Ideal Gas

	Rev.	Rev., No phase change		Rev. Isothermal	Rev. Adiabatic
		const. ext. P, p_{ext}	final P, p_f		
w	$- \int P dV$	$- p_{ex} \Delta V$	$- p_f \Delta V$	$- nRT \ln \frac{V_2}{V_1}$	$= \int C_V(T) dT$
q	$\Delta U - w$			$nRT \ln \frac{V_2}{V_1}$	0
ΔU	$= \int C_V(T) dT$			0	$= \int C_V(T) dT$
ΔH	$= \int C_p(T) dT$			0	$= \int C_p(T) dT$

Thermodynamic Response Functions

Appendix

Property	PD	Value for Perfect Gas	Info:
Internal Pressure	$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$	$\pi_T = 0$	Strength/nature of interactions between molecules
Expansion Coefficient	$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$	$\alpha = 1 / T$	The higher T , the less responsive is its volume to a change in temperature
Isothermal Compressibility	$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$	$\kappa_T = 1 / p$	The higher the p , the lower its compressibility
Joule-Thomson Coefficient	$\mu = \left(\frac{\partial T}{\partial p} \right)_H$	$\mu = 0$	Another indication of molecular interactions.