

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 $\Delta U = \oint dU = 0 \Rightarrow q + w = 0$

Measuring the Change in Internal Energy

$$\Delta U = q + w$$

Constant volume process

$$\Delta U = q \quad (w = 0)$$

Estimate q with a calorimeter

Adiabatic process

$$\Delta U = w \quad (q = 0)$$

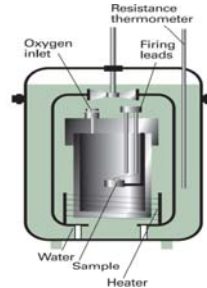
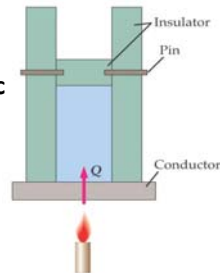
Estimate w as pV work

Variation of Internal Energy U with System Properties

- Variation with temperature at constant volume

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

Schematic diagram



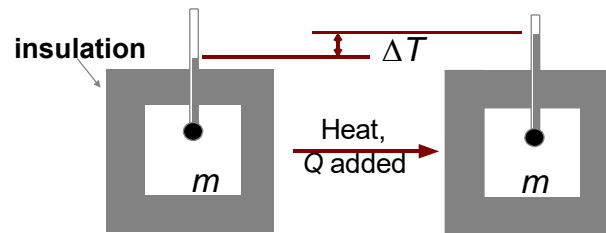
Adiabatic bomb calorimeter

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

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

Variation of Internal Energy U with System Properties

- Variation with temperature at constant volume



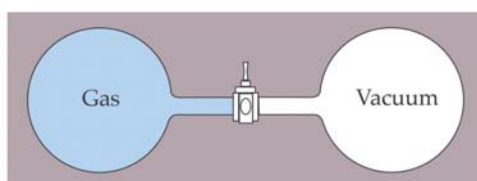
- Heat is added to a substance of mass m in a **fixed volume** enclosure, which causes a change in internal energy, U . Thus,

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

The subscript **V** implies **constant volume**

Variation of Internal Energy U with System Properties

- 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

$$\begin{aligned}\delta w &= 0 \\ \delta q &= 0 \\ dU_T &= \left(\frac{\partial U}{\partial V}\right)_T dV = 0 \\ dV \neq 0 &\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0 \\ &\text{for an ideal gas}\end{aligned}$$

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

Closed systems

Variation of Internal Energy U with System Properties

- Variation with volume at constant temperature $\left(\frac{\partial U}{\partial V}\right)_T$

$$\text{Let } U = U(T, V) \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V = -1$$

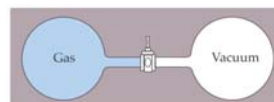
$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V = -\mu_J C_V$$

Internal pressure

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

By the design of Joule's experiment,

$$\Delta U = q + w \text{ with } q = 0, w = 0 \Rightarrow \Delta U = 0$$



In general, a plot of T vs V from Joule's setup gives

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$$

Variation of Internal Energy U with System Properties

- Variation with temperature at constant pressure

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

$$\therefore \left(\frac{\partial U}{\partial T}\right)_p = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = C_V \left[1 - \mu_J \left(\frac{\partial V}{\partial T}\right)_p\right]$$

Let us define the **isobaric expansion coefficient**

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

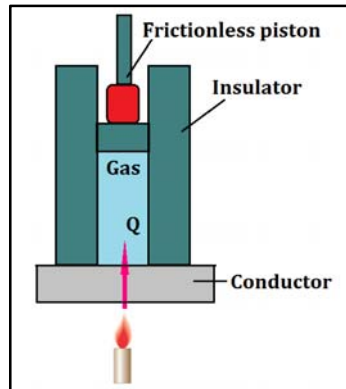
Thus,

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V [1 - \alpha \mu_J V]$$

Summary: Internal Energy

- Internal energy, U of a system is the total of kinetic and potential energies of all its constituent particles
- $dU = 0$ for an isolated system at equilibrium
- $dU = C_V dT + \pi_T dV$ where $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = -\mu_J C_V$
- 1st law of thermodynamics: $\Delta U = q + w$; $dU = \delta q + \delta w$
- For constant volume processes, $Q_v = \Delta U = m C_V \Delta T$
- For an ideal gas, $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$ and $U = U(T)$ (closed system).

Heat Transaction at Constant Pressure



Enthalpy and heat

- Let us define **enthalpy** as

$$H = U + pV$$

- 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,**

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

For a finite isobaric process,

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

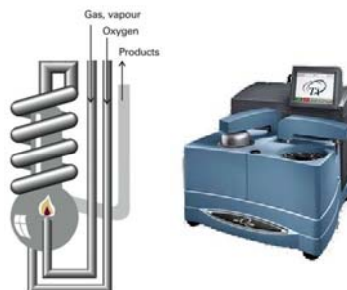
$$\Delta H = Q_p$$

Enthalpy and heat

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

Enthalpy changes are measured using

- isobaric calorimeter
- differential scanning calorimeter
- adiabatic flame calorimeter



Molar specific heat at constant pressure, $C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p$

$$\therefore dH = C_{p,m} dT$$

In several experimental measurements,

$$C_{p,m} = f(T) = a + bT + \frac{c}{T^2} \Rightarrow \Delta H = Q_p = n \int_{T_1}^{T_2} C_{p,m} dT$$

Enthalpy and the Ideal Gas

- By definition, $dH = dU + d(pV)$

- For an ideal gas, $pV = nRT$

$$\therefore dH = dU + Rdn$$

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

$$dH = dU + RTd(n) \Rightarrow \Delta H = \Delta U + (\Delta n)RT$$

- For a non-reactive ideal gas undergoing heating/ cooling in a closed vessel

$$dH = dU + nRdT \Rightarrow \Delta H = \Delta U + nR\Delta T = (C_p + nR)\Delta T$$

$$\Delta H = C_p\Delta T$$

Variation of Enthalpy with System Variables

- Variation with temperature at constant pressure

$$c_p = \left(\frac{\partial H}{\partial T} \right)_p \quad dH = c_p dT \quad \Delta H = Q_p = c_p \Delta T$$

In general, for a closed system

$$H = H(p, T)$$

$$dH = c_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

Variation of Enthalpy with System Variables

- Variation with pressure at constant temperature

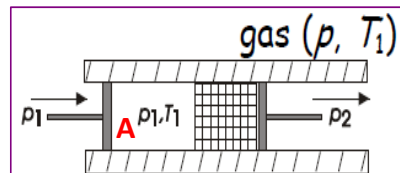
$$H = H(p, T)$$

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

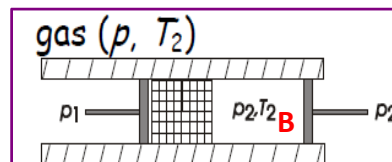
$$\therefore \left(\frac{\partial H}{\partial p} \right)_T = - \left(\frac{\partial T}{\partial p} \right)_H \left(\frac{\partial H}{\partial T} \right)_p = -\mu_{JT} c_p$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H \quad \text{Joule Thomson coefficient}$$

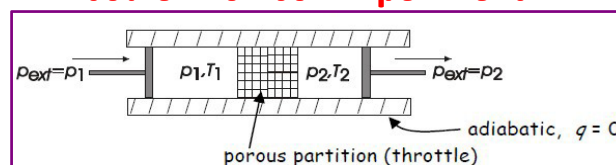
Joule Thomson Experiment



- The gas in **A** is **compressed isothermally** under **constant pressure p_1** so that its **volume** changes from **V_1 to 0**
- After crossing the porous plug, the gas in **B** **expands** against a **constant pressure p_2** ($p_1 > p_2$) so that its **volume** increases from **0 to V_2**
- **Boundary of the system moves** with the gas and encloses the **same mass of gas**



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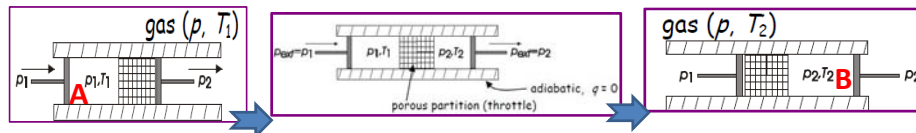
For this experiment, $q = 0 \Rightarrow \Delta U = U_2 - U_1 = w$

$$w = -p_1(0 - V_1) - p_2(V_2 - 0) = p_1V_1 - p_2V_2$$

Thus, $U_2 - U_1 = p_1V_1 - p_2V_2 \Rightarrow U_2 + p_2V_2 = U_1 + p_1V_1$

$$\therefore H_2 = H_1$$

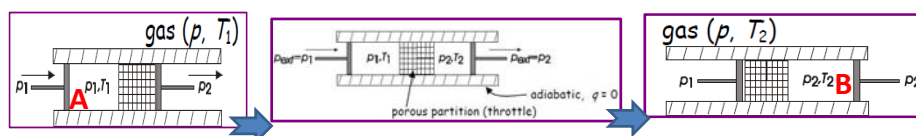
Joule Thomson Experiment



Isenthalpic expansion of a gas from a region of constant high pressure to a region of constant low pressure through a porous plug

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H \approx \frac{\Delta T}{\Delta p} \quad \text{under isenthalpic condition}$$

Joule Thomson Experiment



- The gas in **A** is **compressed isothermally** under constant pressure p_1 so that its **volume** changes from V_1 to 0
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Variation of Enthalpy with System Variables

- Variation with pressure at constant temperature

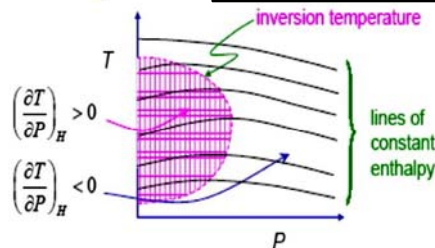
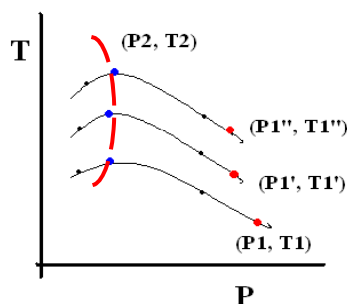
$$H = H(p, T)$$

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

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

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H \quad \text{Joule Thomson coefficient}$$

Joule Thomson Experiment



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

μ_{JT}	ΔT	Remark
positive	negative	Gas cools on expansion
negative	positive	Gas heats on expansion

The "inversion temperature"

On a (T, p) isenthalpic plot, this is the point where μ_{JT} changes sign from + to -

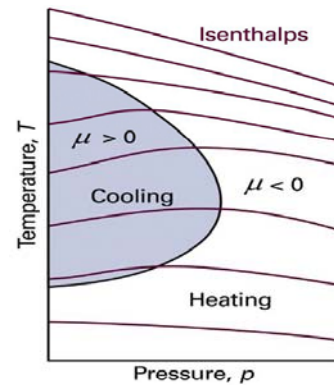
For a real gas $\mu_{JT} \neq 0$

(except at the maximum inversion temperature)

Joule Thomson Experiment

Gas **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.

For a van der Waals gas, $\mu_{JT} = \frac{1}{c_p} \left(\frac{2a}{RT} - b \right)$

Changes in U and H

are measured in terms of

Thermodynamic Response Functions

Thermodynamic Response Functions

These are **measurable quantities** that can be obtained from experiments involving variation of **p, V, T** of closed systems

Response function	Definition
Specific heat at constant volume	$c_v = \left(\frac{\partial U}{\partial T} \right)_v$
Specific heat at constant pressure	$c_p = \left(\frac{\partial H}{\partial T} \right)_p$
Isobaric expansion coefficient	$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$
Joule coefficient	$\mu_J = \left(\frac{\partial T}{\partial V} \right)_U$
Joule Thomson coefficient	$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H$

Estimating ΔU and ΔH during change in state

Change in internal energy $U = U(T, V)$

- Constant volume process $\Delta U = Q_v = c_v \Delta T$
- Constant temperature process $\Delta U = -\mu_J c_v \Delta V$
- With change in both T and V $\Delta U = c_v \Delta T - \mu_J c_v \Delta V$

Change in enthalpy $H = H(T, p)$

- Constant pressure process $\Delta H = Q_p = c_p \Delta T$
- Constant temperature process $\Delta H = -\mu_{JT} c_p \Delta p$
- With change in both T and p $\Delta H = c_p \Delta T - \mu_{JT} c_p \Delta p$

Thermodynamic Response Functions for an Ideal Gas

Response function	Ideal gas behaviour
Specific heat at constant volume $C_V = \left(\frac{\partial U}{\partial T}\right)_V$	$\frac{3}{2}R$
Specific heat at constant pressure $C_p = \left(\frac{\partial H}{\partial T}\right)_P$	$\frac{5}{2}R$
Isobaric expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$	$1/T$
Joule coefficient $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$	0
Joule Thomson coefficient $\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$	0

Homework

By studying the equation of state of a closed system, it is possible to express pressure as

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

Use the cyclic rule of partial derivatives to show that

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

where two thermodynamic response functions have been used

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

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

A sample consisting of 65.0 g of Xe is confined in a container at 2.0 atm and 298 K.
 (Atomic weight of Xe is 131; $C_p = 5R/2$)
 Calculate ΔU and ΔH if the gas undergoes expansion under isothermal/adiabatic conditions
 (a) Reversibly to a pressure of 1 atm
 (b) Against a pressure of 1 atm

Nature of expansion		Final equilibrium state	ΔU (J)	ΔH (J)
Isothermal	Reversible			
Isothermal	Irreversible			
Adiabatic	Reversible			
Adiabatic	Irreversible			

Work done by adiabatic expansion of an Ideal gas

$$dU = \delta q + \delta w, \delta q = 0 \Rightarrow \delta w = dU = n C_V dT$$

$$w = - \int_1^2 p_{ext} dV = n C_V (T_2 - T_1)$$

Reversible adiabatic expansion

Obtain T_2 using any of the following

$$pV^\gamma = \text{constant} \quad \text{or} \quad TV^{\gamma-1} = \text{constant} \quad \text{or} \quad T^\gamma p^{1-\gamma} = \text{constant}$$

Irreversible adiabatic expansion against a constant pressure $p_{ext} = p_2$

Obtain T_2 as follows

$$n C_V (T_2 - T_1) = -p_{ext}(V_2 - V_1) = -p_2 \left(\frac{nRT_2}{p_2} - \frac{nRT_1}{p_1} \right)$$

$$\therefore T_2 = T_1 \frac{\frac{C_V}{R} + \frac{p_2}{p_1}}{\frac{C_V}{R} + 1}$$

1st law of Thermodynamics

Information from the 1st law

- The concept of **internal energy and enthalpy**
- **Constant total energy** of the system plus surroundings during any change in state
- **Transfer/transformation of energy** between system and surrounding, keeping the total energy fixed.

Limitation of the 1st law

- Will the change in state take place?
- If yes, what will be the **spontaneous direction of change**?
- What will be the **new equilibrium state**? **Under what condition will the change stop**?

$$dU_{\text{universe}} = dU_{\text{system}} + dU_{\text{surrounding}} = 0$$

Limitations of the First Law of Thermodynamics

The first law assures us that the total energy of system plus surroundings remains constant during the reaction. Energy can be transferred/transformed, keeping the total energy fixed.

$$dU_{\text{universe}} = dU_{\text{system}} + dU_{\text{surrounding}} = 0$$

Does not say:

Whether energy will get transferred / transformed?

If yes, in which direction?

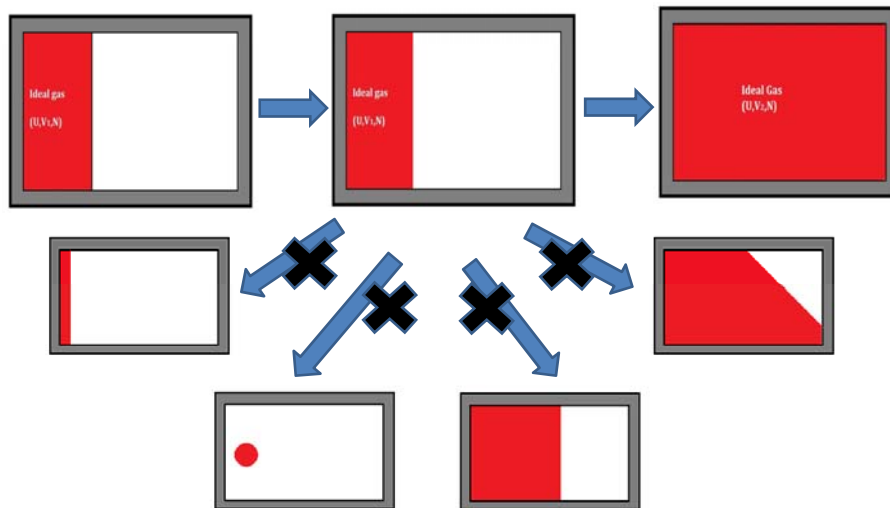
If yes, how long?

If yes, how fast?

Limitations of the 1st law of Thermodynamics

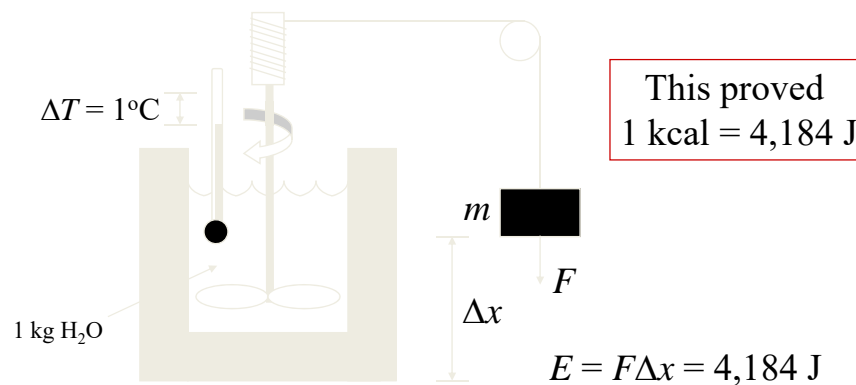
Initial equilibrium state

Final equilibrium state



Converting Heat into Work

- From the 1st law, when $\Delta U = 0$, $q = -w$. So heat supplied to a system can be **completely** converted to work!!
- Such possibility is tested by the construction of **heat engines**



Joule's Mechanical Equivalent of Heat

Second Law of Thermodynamics

- A **spontaneous process** occurs naturally and needs no external source of work.
- A **non-spontaneous process**, although allowed by the 1st law, requires an external source of work to drive it.
- The 2nd law of thermodynamics tells us
 - the **direction of a spontaneous change in state**
 - the **new equilibrium state achieved** at the end of the change

Converting Heat into Work

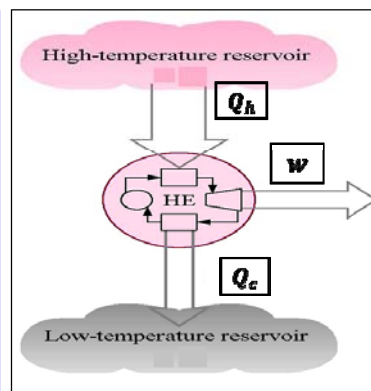
An engine is a device (system) that converts energy to work.

A **heat engine**

- **draws heat from a hot reservoir,**
- **converts some heat to work,** and
- **releases some heat to a cold reservoir.**

The engine itself is a system that undergoes a **cyclic process**

A **reservoir** is a large body whose temperature does not change when it absorbs or gives up heat



Efficiency of the heat engine

$$\eta = \frac{|w|}{Q_h}$$

Heat Engine

An **engine** is a device (system) that converts energy to work.

A heat engine draws heat from a hot reservoir, converts some heat to work, and releases some heat to a cold reservoir.

The engine itself is a system that undergoes a cyclical process

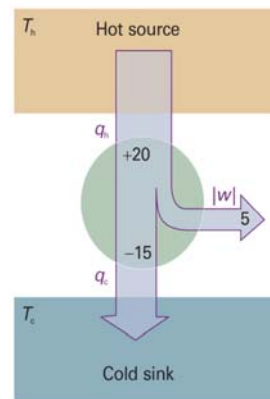
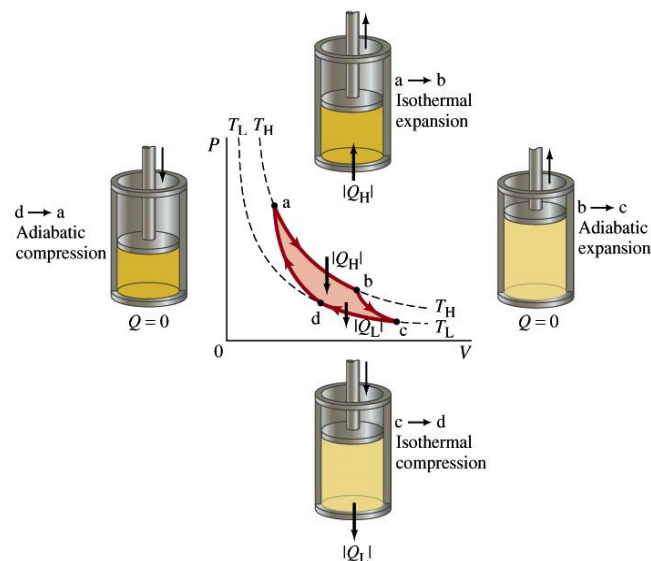
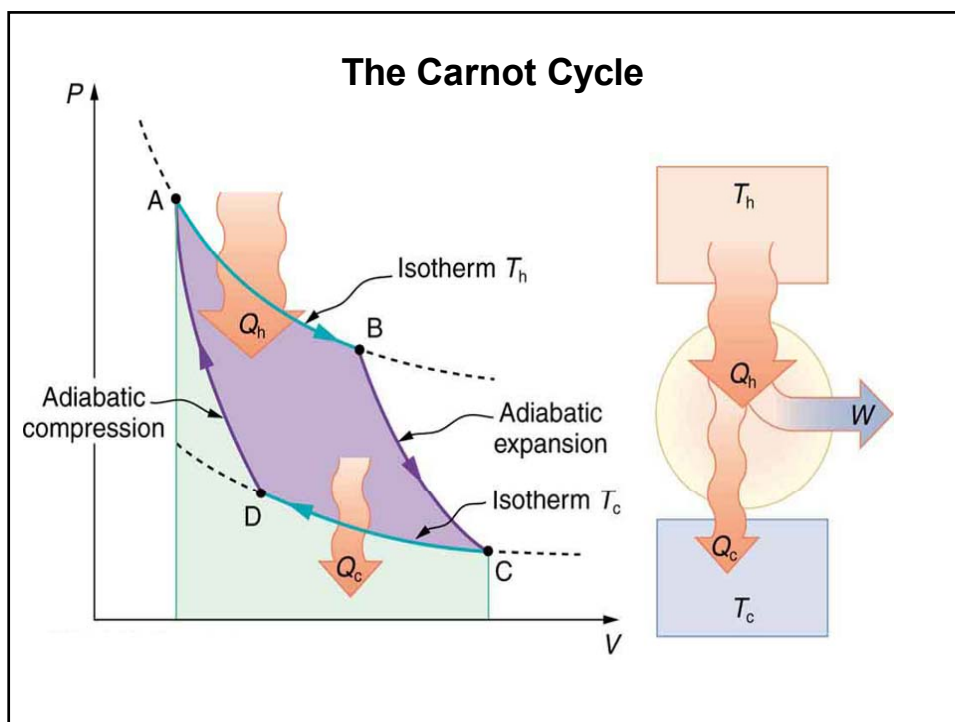


Fig. 3.7 Suppose an energy q_h (for example, 20 kJ) is supplied to the engine and q_c is lost from the engine (for example, $q_c = -15$ kJ) and discarded into the cold reservoir. The work done by the engine is equal to $q_h + q_c$ (for example, $20 \text{ kJ} + (-15 \text{ kJ}) = 5 \text{ kJ}$). The efficiency is the work done divided by the energy supplied as heat from the hot source.

The Carnot Cycle





Carnot Cycle: Four steps

	STEP 1 (A to B)	STEP 2 (B to C)	STEP 3 (C to D)	STEP 4 (D to A)
	ISOTHERMAL EXPANSION	ADIABATIC EXPANSION	ISOTHERMAL COMPRESSION	ADIABATIC COMPRESSION
w	$-nRT_H \ln \frac{V_B}{V_A}$			
ΔU	0			
q	$nRT_H \ln \frac{V_B}{V_A}$			
$\frac{q_{rev}}{T}$				

Carnot Cycle: Four steps

- Isothermal expansion: A to B
- Adiabatic expansion: B to C
- Isothermal compression: C to D
- Adiabatic compression: D to A

$$w_1 = -nRT_H \ln \frac{V_b}{V_a}$$

$$dU = 0$$

$$w_1 = -q_1$$

$$T_H V_b^{\gamma-1} = T_c V_c^{\gamma-1}$$

$$w_2 = nC_V (T_c - T_H)$$

$$q_2 = 0$$

$$w_3 = -nRT_c \ln \frac{V_d}{V_c}$$

$$dU = 0$$

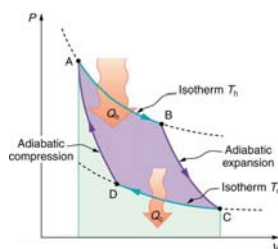
$$w_3 = -q_3$$

$$T_H V_a^{\gamma-1} = T_c V_d^{\gamma-1}$$

$$w_4 = nC_V (T_H - T_c)$$

$$q_4 = 0$$

Carnot Engine



$$TV^{\gamma-1} = \text{const.};$$

$$T_H V_B^{\gamma-1} = T_c V_C^{\gamma-1} \quad T_H V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \quad \left(\frac{V_B}{V_A}\right) = \left(\frac{V_C}{V_D}\right)$$

$$\ln(V_D/V_C) = -\ln(V_B/V_A)$$

Step	1 (A → B)	2 (B → C)	3 (C → D)	4 (D → A)	Total (A → B → C → D → A)
w	$-nRT_H \ln \left(\frac{V_B}{V_A}\right)$	$C_V (T_c - T_H)$	$-nRT_c \ln \left(\frac{V_D}{V_C}\right)$	$C_V (T_H - T_c)$	$-nR(T_H - T_c) \ln \left(\frac{V_B}{V_A}\right)$
q	$nRT_H \ln \left(\frac{V_B}{V_A}\right)$	0	$nRT_c \ln \left(\frac{V_D}{V_C}\right)$	0	$nR(T_H - T_c) \ln \left(\frac{V_B}{V_A}\right)$
ΔU	0	$C_V (T_c - T_H)$	0	$C_V (T_H - T_c)$	0
$\frac{q_{rev}}{T}$	$nR \ln \left(\frac{V_B}{V_A}\right)$	0	$nR \ln \left(\frac{V_D}{V_C}\right)$	0	0

Efficiency of Carnot Engine

For any cyclic engine, $\Delta U = 0 \Rightarrow |w| = |Q| = |Q_h + Q_c|$

Thus, by definition $\eta = \frac{|w|}{Q_h} = \frac{Q_h + Q_c}{Q_h}$ i.e. $\eta = 1 + \frac{Q_c}{Q_h}$

As the Carnot engine works **reversibly** and employs **an ideal gas**,

$$Q_H = nRT_h \ln\left(\frac{V_B}{V_A}\right) \quad \text{and} \quad |w| = nR(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)$$

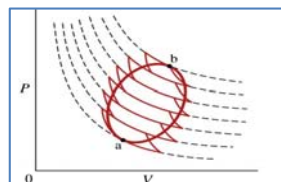
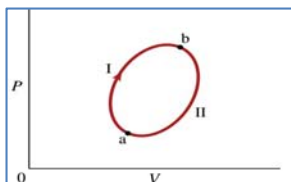
$$\therefore \eta = \frac{|w|}{Q_H} = \frac{T_h - T_c}{T_h} \quad \text{i.e.} \quad \span style="border: 1px solid red; padding: 2px;"> $\eta = 1 - \frac{T_c}{T_h}$$$

Note: $1 + \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \Rightarrow \span style="border: 1px solid blue; border-radius: 50%; padding: 2px;"> $\frac{Q_h}{T_h}$ + $\frac{Q_c}{T_c}$ = 0$

Isothermal, absorption of heat at T_h

Isothermal, release of heat at T_c

Entropy



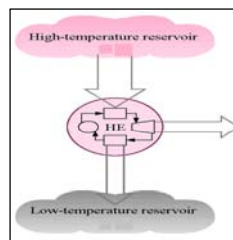
- Over one cycle of Carnot Engine, $\oint \frac{\delta q_{rev}}{T} = \frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$
- Since any **reversible cycle** can be approximated by a **series of Carnot cycles**,

$$\oint \frac{\delta q_{rev}}{T} = 0 \quad \text{along any reversible cyclic path}$$
- A state function called **entropy, S** is identified such that
 - $dS = \frac{\delta q_{rev}}{T}$ is an **exact differential**
 - $\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{\delta q_{rev}}{T}$ is **independent of the path**.

Entropy Change in Non-isolated Systems

- $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- All natural processes are cyclic and irreversible.

$$\therefore \Delta S_{\text{universe}} > 0$$



Consider an **irreversible engine** that

- absorbs Q_h^* heat at T_h
- undergoes **irreversible isothermal expansion** at T_h
- has the same steps as Carnot engine otherwise

$$\frac{Q_h^*}{T_h} + \frac{Q_c}{T_c} < 0$$

At the end of the cycle, the working system is restored to its initial state

$$\Delta S_{\text{sys}} = 0$$

$$\Delta S_{\text{surr}} = -\frac{Q_h^*}{T_h} - \frac{Q_c}{T_c} > 0$$

$$\therefore \Delta S_{\text{universe}} > 0$$

Key Questions about Entropy

- Can we estimate the change in entropy, ΔS for different processes?
- Can entropy be used to predict the following?
 - ✓ the direction of spontaneous change
 - ✓ the condition of equilibrium

Simple test cases

By definition

$$dS = \frac{\delta q_{rev}}{T} \quad \text{and} \quad \Delta S = \int_1^2 \frac{\delta q_{rev}}{T}$$

For any isothermal process

$$\Delta S = \int_1^2 \frac{\delta q_{rev}}{T} = \frac{1}{T} \int_1^2 \delta q_{rev} \quad \therefore \Delta S = \frac{Q_{rev}}{T}$$

For an isothermal expansion of an ideal gas

$$\Delta U = 0 \Rightarrow Q_{rev} = -w_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

Simple test cases

By definition

$$dS = \frac{\delta q_{rev}}{T} \quad \text{and} \quad \Delta S = \int_1^2 \frac{\delta q_{rev}}{T}$$

For an isochoric reversible process

$$\delta w_{rev} = 0 \Rightarrow dU = \delta q_v = C_v dT$$

$$\Delta S = \int_1^2 \frac{\delta q_v}{T} = C_v \int_1^2 \frac{dT}{T}$$

$$\therefore \Delta S = C_v \ln \left(\frac{T_2}{T_1} \right)$$

Estimation of change in entropy

Simple test cases

- For a **reversible** process involving changes in T and V of 1 mole of an ideal gas

$$\delta q_{rev} = dU + p dV \Rightarrow \frac{\delta q_{rev}}{T} = \frac{dU}{T} + \frac{p}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

$$\int_1^2 dS = S_2 - S_1 = \Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$$

Estimation of change in entropy

Simple test cases

- For a **reversible** process $(T_1 \ V_1 \ N) \rightarrow (T_2 \ V_2 \ N)$

$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$$

- For an **irreversible** process between the same two states

$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$$

This is because

- ✓ entropy S is a state function and
- ✓ ΔS is independent of the path connecting the two states

Simple test cases

By definition

$$dS = \frac{\delta q_{rev}}{T} \quad \text{and} \quad \Delta S = \int_1^2 \frac{\delta q_{rev}}{T}$$

Reversible heating at constant pressure (**no** phase change)

$$\delta q_{rev} = \delta q_p = C_p dT \Rightarrow \Delta S = C_p \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\therefore \Delta S = C_p \ln\left(\frac{T_2}{T_1}\right)$$

Reversible heating at constant pressure (**with** phase change)

$$\Delta S = \frac{Q_{rev}}{T} = \frac{\Delta H}{T}$$

Here, ΔH is the **enthalpy of phase change (latent heat)** at the transition temperature T

Entropy and Clausius Inequality

- For any reversible engine, operating between two temperatures T_h and T_c ,

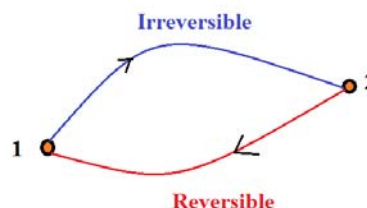
$$\eta_{rev} = \frac{|w_{rev}|}{Q_h} = 1 - \frac{T_c}{T_h}$$

- For any arbitrary engine (**NOT** reversible) operating between the same two temperatures T_h and T_c , with the **same input of Q_h**

$$\eta < \eta_{rev} \quad \text{because} \quad w_{irrev} < w_{rev}$$

$$\therefore 1 + \frac{Q_c}{Q_h} < 1 - \frac{T_c}{T_h} \Rightarrow \frac{Q_h}{T_h} + \frac{Q_c}{T_c} < 0 \Rightarrow \oint \frac{\delta q}{T} < 0$$

Entropy and Clausius Inequality



For any irreversible cycle $\oint \frac{\delta q}{T} < 0$

State 1 $\xrightarrow{\text{Irreversible}}$ State 2 $\xrightarrow{\text{Reversible}}$ State 1

$$\therefore \int_1^2 \frac{\delta q_{\text{irr}}}{T} + \int_2^1 \frac{\delta q_{\text{rev}}}{T} < 0$$

$$\int_1^2 \frac{\delta q_{\text{irr}}}{T} - \int_1^2 dS < 0 \Rightarrow \Delta S = S_2 - S_1 > \int_1^2 \frac{\delta q_{\text{irr}}}{T}$$

Entropy and Clausius Inequality

For an **irreversible change** in state from state 1 to state 2

$$\int_1^2 dS > \int_1^2 \frac{\delta q_{\text{irr}}}{T} \Rightarrow dS > \frac{\delta q_{\text{irr}}}{T}$$

Mathematical statement of 2nd law of thermodynamics

$$dS \geq \frac{\delta q}{T}$$

$dS > \frac{\delta q}{T}$	Irreversible and spontaneous change in state
$dS = \frac{\delta q}{T}$	Reversible process
$dS < \frac{\delta q}{T}$	Process associated with the change in state is NOT permitted

Application to transformations in real systems

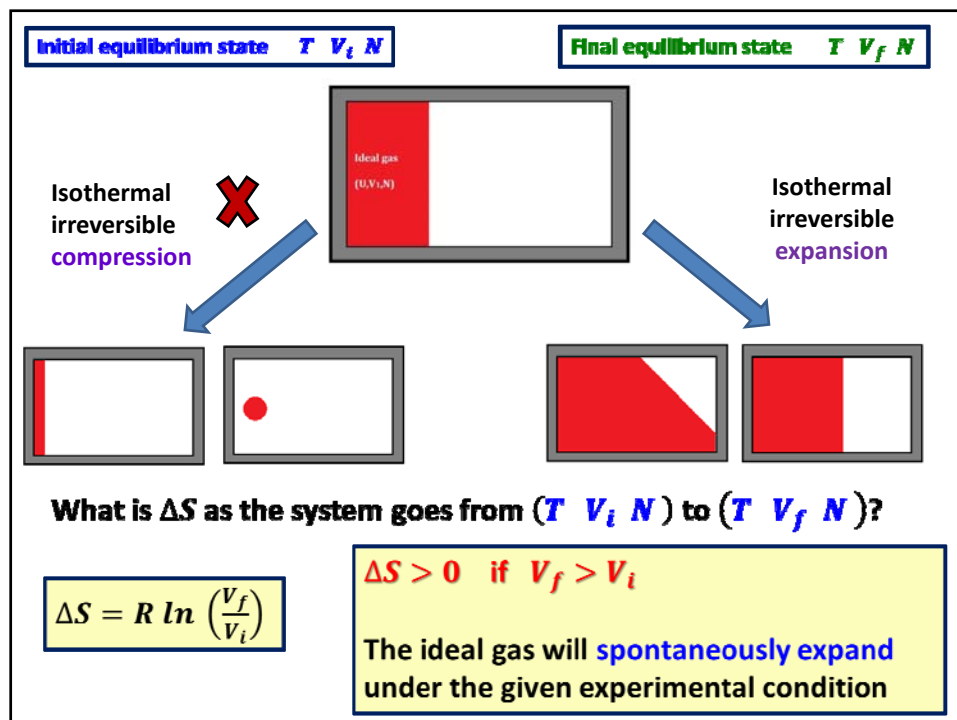
- From Clausius Inequality

$$dS > \frac{\delta q_{irrev}}{T}$$

- In an **isolated system**, during an **irreversible process**,

$$\delta q_{irrev} = 0 \Rightarrow dS > 0$$

- For a real transformation in an **isolated system**, upon withdrawal of an internal constraint, the system **spontaneously changes towards that direction that increases the entropy**.



Initial equilibrium state $T V_i N$ Final equilibrium state $T V_f N$

Isothermal irreversible expansion

Under what condition does the gas **stop expanding** any further so that a **new equilibrium state** is reached?

$\Delta S = R \ln \left(\frac{V_f}{V_i} \right)$

ΔS reaches a maximum when V_f is maximum
 $\Rightarrow S_{final}$ is maximum when $V_f = V_2$
 The ideal gas will **spontaneously expand** till it **fills up the entire available volume**

Entropy Change in an Isolated System

- In the absence of any exchange of heat,

$$dS \geq 0$$
- Upon withdrawal of an internal constraint, the system **spontaneously changes towards that direction that maximizes the entropy.**

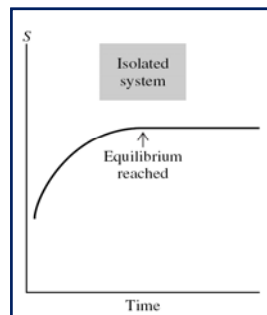
Initial equilibrium state Final equilibrium state

The change in entropy, $\Delta S = nR \ln \left(\frac{V_{final}}{V_1} \right)$ is **maximum** when the final volume, V_{final} is maximum

Therefore, the final equilibrium state is reached when $V_{final} = V_2$

Entropy Change in an Isolated System

- Any **natural change** within an isolated system is accompanied by an **increase in entropy**
- The entropy continues to increase as long as the changes occur within the system
- When **entropy attains its maximum value**, the system reaches a **new equilibrium state**.



$dS > 0$	Irreversible and spontaneous change in state
$dS = 0$	No further change, a new equilibrium is reached
$dS < 0$	Process associated with the change in state is NOT permitted

Entropy and Clausius Inequality

For an **irreversible change** in state from state 1 to state 2

$$\int_1^2 dS > \int_1^2 \frac{\delta q_{irr}}{T} \Rightarrow dS > \frac{\delta q_{irr}}{T}$$

Mathematical statement of 2nd law of thermodynamics

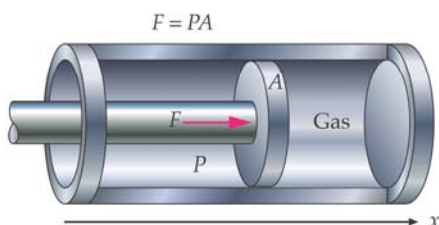
$$dS \geq \frac{\delta q}{T}$$

$dS > \frac{\delta q}{T}$	Irreversible and spontaneous change in state
$dS = \frac{\delta q}{T}$	Reversible process
$dS < \frac{\delta q}{T}$	Process associated with the change in state is NOT permitted

The First Law of Thermodynamics. Application to a particular case:

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.



The work done on the gas in an expansion is

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

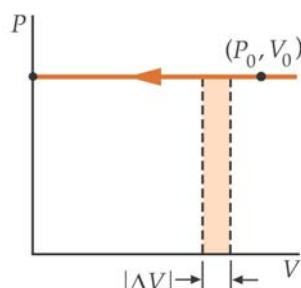
$$W_{on\ gas} = -W_{by\ gas}$$

P- V diagrams

Constant pressure

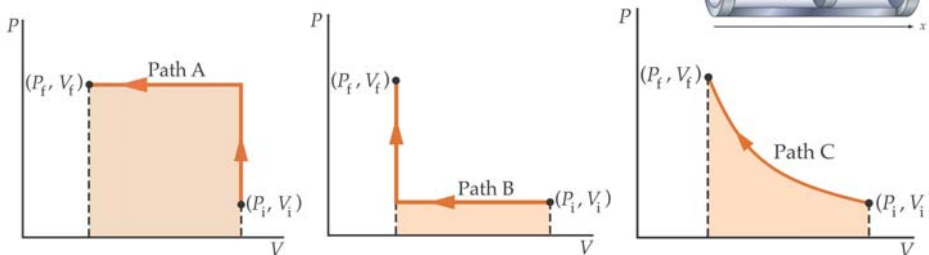
$$W_{on\ gas} = -\int_{V_1}^{V_2} P dV = P(V_1 - V_2)$$

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]



The First Law of Thermodynamics. P-V diagrams

P- V diagrams



Connecting an initial state and a final state by three paths

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

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

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