

# Physical Chemistry

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(Sixth edition)

*Bilingual*

*Program*

# Part 1: Equilibrium

## 3. The First Law: the machinery

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## 3. The First Law: the machinery

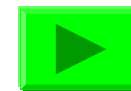
In this chapter we begin to unfold some of the power of thermodynamics by showing how to establish relations between different properties of a system. The procedure we use is based on the experimental fact that the internal energy and the enthalpy are state functions, and we derive a number of relations between observables by exploring the mathematical consequences of these facts.



# 3. The First Law: the machinery

## 3.1 State functions

- 1). Exact and inexact differentials
- 2). Changes in internal energy
- 3). Expansion coefficient



## 3.2 The temperature dependence of the enthalpy

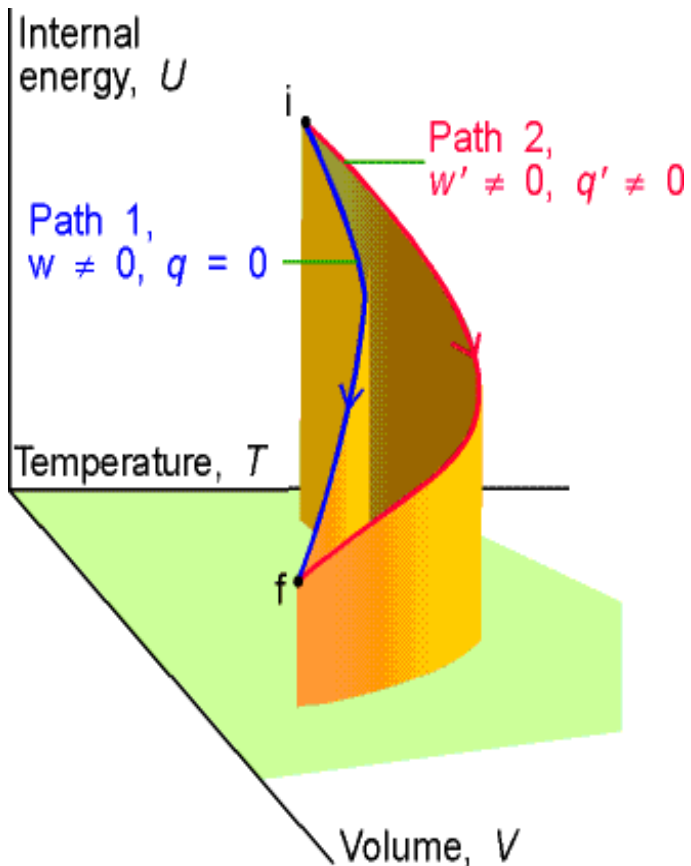
- 1). Changes in enthalpy at constant volume
- 2). The isothermal compressibility
- 3). The Joule -Thomson effect

## 3.3 The reaction between $C_v$ and $C_p$



# 3.1 State functions

## 1). Exact and inexact differential



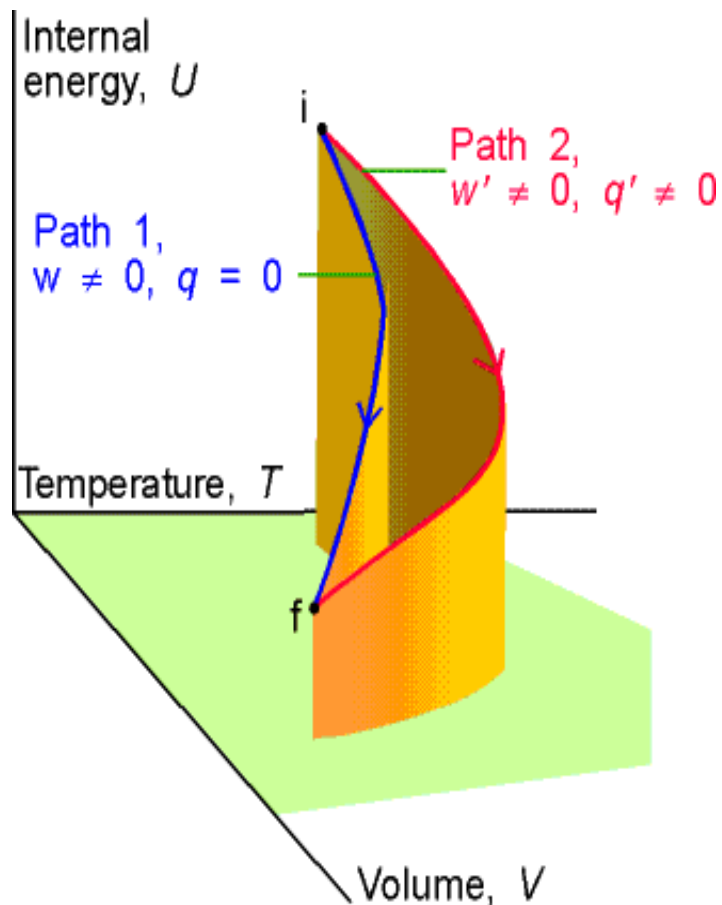
The initial state of the system is **i** and in this state the internal energy is  $U_i$ . Work is done by the system as it expands adiabatically to a state **f**. In this state the system has an internal energy  $U_f$  and the work done on the system as it changes along **Path 1** from **i** to **f** is  $w$ .  $U$  is a property of the state;  $w$  is a property of the path.

$$\Delta U = \int_i^f dU$$



# 3.1 State functions

## 1). Exact and inexact differential



In Path 2, the initial and final states are the same but in which the expansion is not adiabatic. In this path an energy  $q'$  enters the system as heat and the work  $w'$  is not the same as  $w$ . The work and the heat are path functions.

$$q = \int_{i, \text{path}}^f dq$$



## 3.1 State functions

### 1). Exact and inexact differential

$\Delta U$ , independent of the path, an exact differential. An exact differential is an infinitesimal quantity which, when integrated, gives a result that is independent of the path between the initial and final states.

$q$  or  $w$ , dependent on the path, an inexact differential. When a system is heated, the total energy transferred as heat is the sum of all individual contributions at each point of the path.

$$\cancel{\Delta q}$$

$$\cancel{q_f - q_i}$$

$$q$$

$$dq$$

$$d\bar{q}$$



## Example – Calculating work, heat, and internal energy

Consider a perfect gas inside a cylinder fitted with a piston. Let the initial state be  $T, V_i$  and the final state be  $T, V_f$ . The change of state can be brought about in many ways, of which the two simplest are following: Path 1, in which there is free expansion against zero external pressure; Path 2, in which there is reversible, isothermal expansion. Calculate  $w$ ,  $q$ , and  $\Delta U$  for each process.





## Example – Calculating work, heat, and internal energy

**Method:** To find a starting point for a calculation in thermodynamics, it is often a good idea to go back to first principles, and to look for a way of expressing the quantity we are asked to calculate in terms of other quantities that are easier to calculate. Because the internal energy of a perfect gas arises only from the kinetic energy of its molecules, it is independent of volume; therefore, for any **i s o t h e r m a l c h a n g e**, in general  $\Delta U = q + w$ .



## Example – Calculating work, heat, and internal energy

**Answer:** Since  $\Delta U = 0$  for both paths and  $\Delta U = q + w$ .

The work of free expansion is zero,

in Path 1,  $w = 0$  and  $q = 0$ ;

for Path 2, the work is given by

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

so  $w = -nRT \ln (V_f/V_i)$ , and

$$q = nRT \ln (V_f/V_i).$$



## 3.1 State functions

### 2). Changes in internal energy

For a closed system of constant composition,  $U$  is a function of  $V$  and  $T$ . When  $V$  changes to  $V + dV$  at constant  $T$ ,  $U$  changes to

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

When  $T$  changes to  $T + dT$  at constant  $V$ ,  $U$  changes to

$$U' = U + \left(\frac{\partial U}{\partial T}\right)_V dT$$



$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$



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



## 3.1 State functions

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

$$C_V$$

$\left(\frac{\partial U}{\partial T}\right)_V$  the slope of a plot of  $U$  against  $T$  at constant  $V$ .

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

$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$ , the internal pressure, the same dimension as  $p$

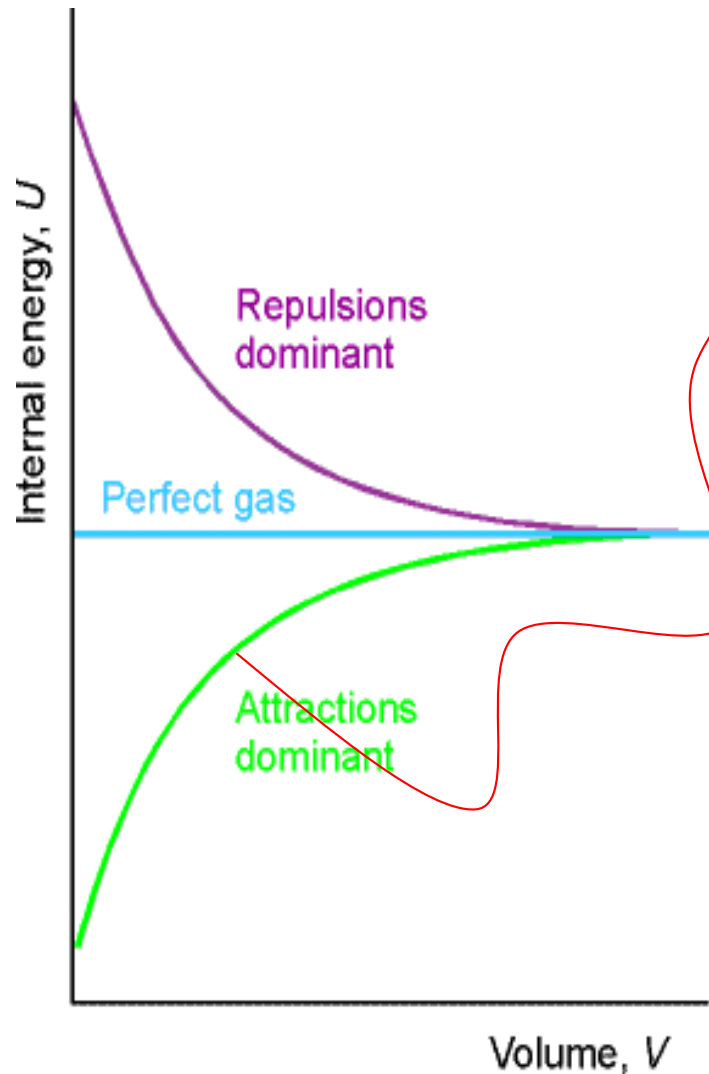
$$dU = \pi_T dV + C_V dT$$

In a closed system of constant composition,  $dU$  is proportional to  $dV$  and  $dT$ , the coefficients of proportionality being the partial derivatives.



# 3.1 State functions

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



If  $dU > 0$  as the volume of the sample expands isothermal,  $dV > 0$ , which is the case when there are attractive forces between the particles  $\pi_T > 0$

When there are no interactions between the molecules,  $U$  is independent of their separation and hence independent of the volume the sample occupies; hence  $\pi_T = 0$  for a perfect gas.



## 3.1 State functions

### 3). Changes in enthalpy at constant pressure

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

Dividing both sides of the equation by  $dT$ , it follows that:

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

The expansion coefficient,  $\alpha$ , is expressed as:

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

A large value of  $\alpha$  means that the volume of the sample responds strongly to changes in temperature



## 3.1 State functions

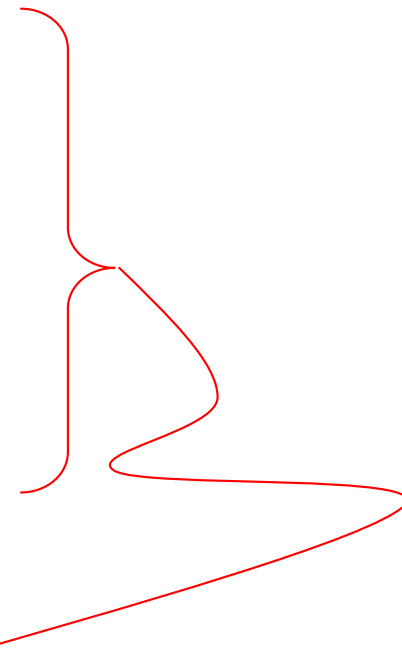
### 3). expansion coefficient

Introducing the definition of  $\alpha$  into the equation:

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

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

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





## 3.1 State functions

### 3). expansion coefficient

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

For a perfect gas,  $\pi_T=0$ :

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

The constant-volume heat capacity of a perfect gas is equal to the slope of a plot of internal energy against temperature at constant pressure as well as to the slope at constant volume.





## Example

Derive an expression for the expansion coefficient for a perfect gas by using the expansion coefficient of a gas.

**Method:** To use the expression of the expansion coefficient of a gas, we simply substitute the expression for  $V$  in terms of  $T$  obtained from the equation of state for the gas. The pressure is treated as a constant.

**Answer:** Because  $pV = nRT$

$$\alpha = \frac{1}{V} \left( \frac{\partial (nRT / p)}{\partial T} \right)_p = \frac{nR}{pV} = \frac{1}{T}$$

The higher the temperature, the less responsive is its volume to a change in temperature.



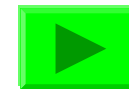
# 3. The First Law: the machinery

## 3.1 State functions

- 1). Exact and inexact differentials
- 2). Changes in internal energy
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## 3.2 The temperature dependence of the enthalpy

- 1). Changes in enthalpy at constant volume
- 2). The isothermal compressibility
- 3). The Joule -Thomson effect



## 3.3 The reaction between $C_V$ and $C_p$



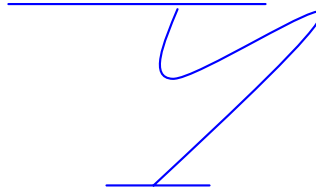
## 3.2 The temperature dependence of the enthalpy

### 1). Changes in enthalpy at constant volume

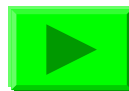
For a closed system of constant composition,  $H$  is a function of  $p$  and  $T$ , and it follows that

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

and

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


This expression implies that:





## 3.2 The temperature dependence of the enthalpy

$$\left( \frac{\partial H}{\partial T} \right)_V = \left( 1 - \frac{\alpha \mu}{\kappa_T} \right) C_p$$

The isothermal compressibility,  $\kappa_T$ , is defined as:

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

The Joule-Thomson coefficient,  $\mu$ , is defined as:

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



## 3.2 The temperature dependence of the enthalpy

### 2). The isothermal compressibility

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

The negative sign in the definition of  $\kappa_T$  ensures that it is positive, because an increase of pressure, implying a positive  $dp$ , brings about a reduction of volume, a negative  $dV$ . For a perfect gas

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial (nRT/p)}{\partial p} \right)_T = -\frac{nRT}{V} \left( \frac{1}{p^2} \right) = \frac{1}{p}$$

It shows that the higher the pressure of the gas, the lower its compressibility.



## Example– Using the isothermal compressibility

The isothermal compressibility of water at 20°C and 1 atm is  $4.94 \times 10^{-6} \text{ atm}^{-1}$ . What change of volume occurs when a sample of volume  $50 \text{ cm}^3$  is subjected to an additional 1000 atm at constant temperature?

**Method:** for an infinitesimal change of pressure at constant temperature, from the definition of  $\kappa_T$ , the volume changes:

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



## Example – Using the isothermal compressibility

**Answer: Integrate both sides:**

$$\int_{V_i}^{V_f} dV = - \int_{p_i}^{p_f} k_T V dp$$

Suppose that  $k_T$ , and  $V$  are approximately constant over the range of pressures of interest:

$$\int_{V_i}^{V_f} dV = - \int_{p_i}^{p_f} k_T V dp$$

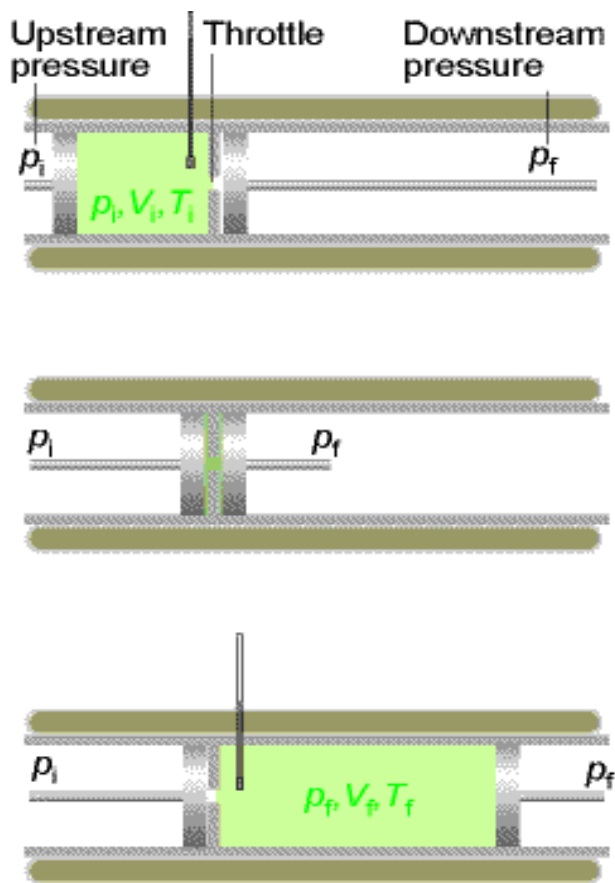
$$\Delta V = -k_T V \int_{p_i}^{p_f} dp = -k_T V \Delta p$$

$$\begin{aligned} \Delta V &= -(4.94 \times 10^{-6} \text{ atm}^{-1}) \times (50 \text{ cm}^3) \times (1000 \text{ atm}) \\ &= -0.25 \text{ cm}^3 \end{aligned}$$



## 3.2 The temperature dependence of the enthalpy

### 3). The Joule -Thomson effect



The thermodynamic basis of Joule - Thomson expansion.

**Adiabatic expansion, Constant  $H$ :**

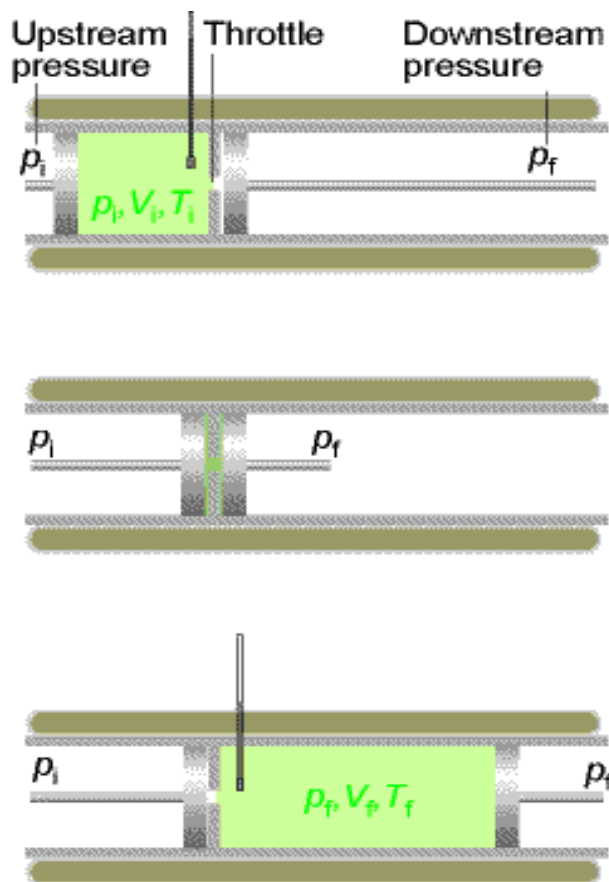
let a gas expand through a porous barrier from one constant pressure to another, and monitored the difference of  $T$  that arose from the expansion. The process was adiabatic. It was observed a lower  $T$  on the low-pressure side, the difference in  $T$  being proportional to the  $p$  difference maintained. This cooling by adiabatic expansion is now called the **Joule-Thomson effect**.





## 3.2 The temperature dependence of the enthalpy

### 3). The Joule -Thomson effect



The thermodynamic basis of Joule -Thomson expansion.

Because all changes to the gas occur adiabatically:  $q = 0$ .

The gas on the left is compressed isothermally and the work done:

$$w_L = - p_i (0 - V_i) = p_i V_i$$

The work done in right:

$$w_R = - p_f (V_f - 0) = -p_f V_f$$

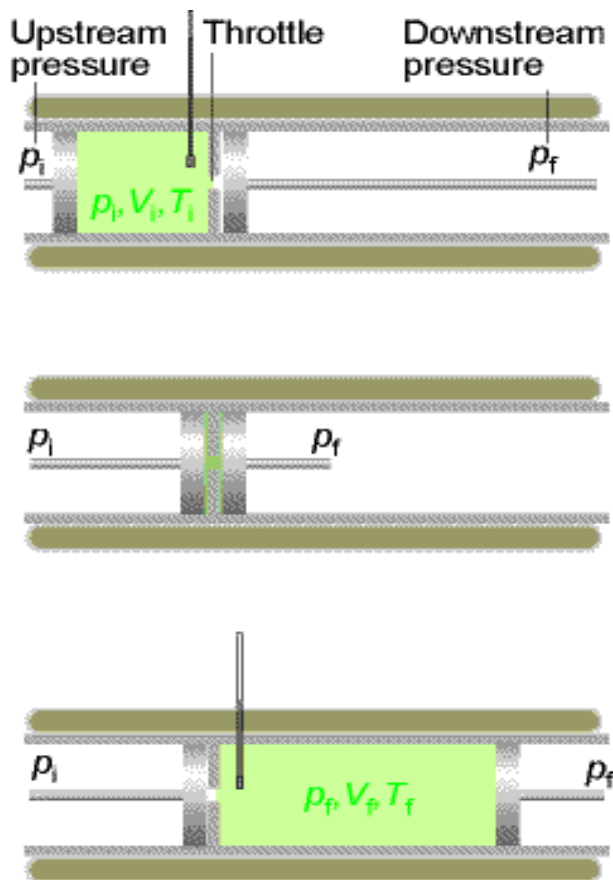
The total work done:

$$w = w_L + w_R = p_i V_i - p_f V_f$$



## 3.2 The temperature dependence of the enthalpy

### 3). The Joule -Thomson effect



The thermodynamic basis of Joule - Thomson expansion.

Since  $q = 0$ , then  $U = w + q = w$ .  
the change of  $U$  of the gas as it moves from one side of the throttle to the other is:

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

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

$$H_f = H_i$$

The expansion occurs without change of enthalpy: an isenthalpic process.



## 3.2 The temperature dependence of the enthalpy

### 3). The Joule -Thomson effect

The property is the ratio of the  $T$  change to the change of  $p$ ,  $\Delta T / \Delta p$ . Adding the constraint of constant enthalpy and taking the limit of small  $\Delta p$  implies the quantity measured is  $(dT/dp)_H$ , which is the **Joule-Thomson coefficient**,  $\mu$ . And  $\mu$  is the ratio of the change in temperature to the change in pressure when a gas expands under adiabatic conditions.

$$\mu = \left( \partial T / \partial p \right)_H$$

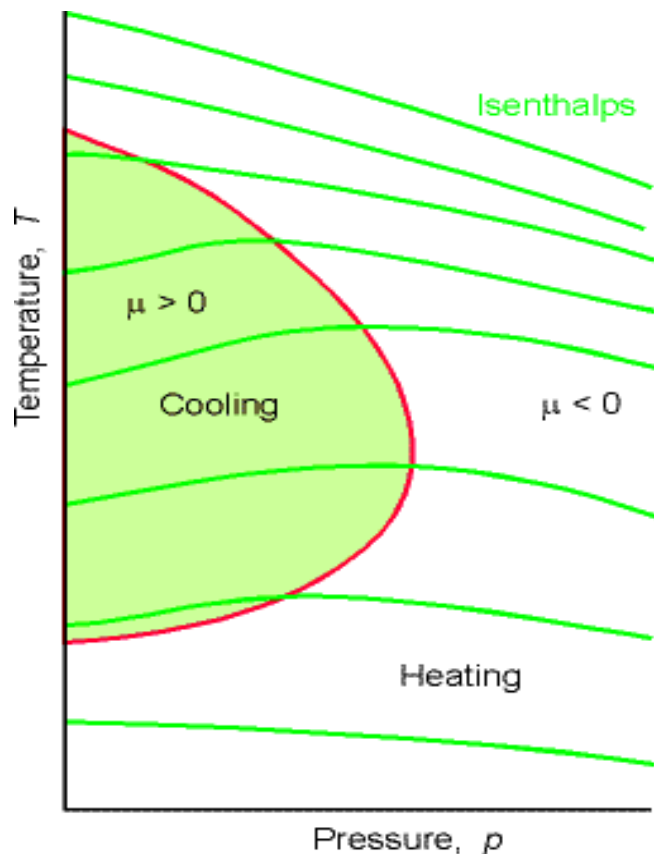
For measurement, the **isothermal Joule-Thomson coefficient**,  $\mu_T$ , is used:

$$\mu_T = \left( \partial H / \partial p \right)_T = -C_p \mu$$



## 3.2 The temperature dependence of the enthalpy

### 3). The Joule -Thomson effect: for real gases



The sign of the Joule-Thomson coefficient,  $\mu$

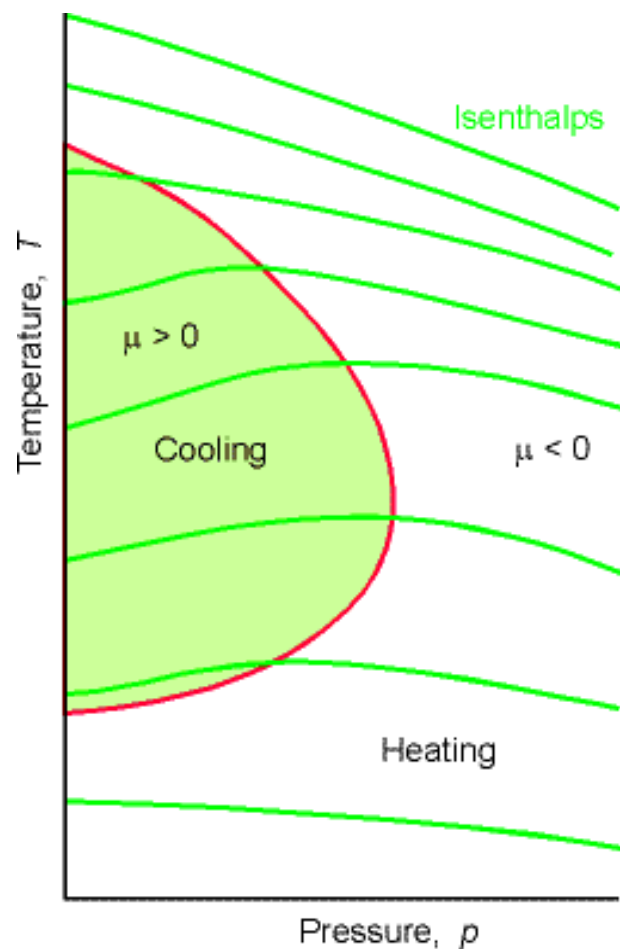
For a perfect gas,  $\mu = 0$ . But Real gases have nonzero  $\mu$  and, depending on the identity of the gas,  $p$  and  $T$ , the relative magnitudes of the attractive and repulsive intermolecular forces, the sign of the coefficient may be either positive or negative.

A **positive sign** implies that  $dT$  is negative when  $dp$  is negative, in which case the gas **cools** on expansion. A **negative sign** implies **heating** process.



## 3.2 The temperature dependence of the enthalpy

### 3). The Joule -Thomson effect: for real gases

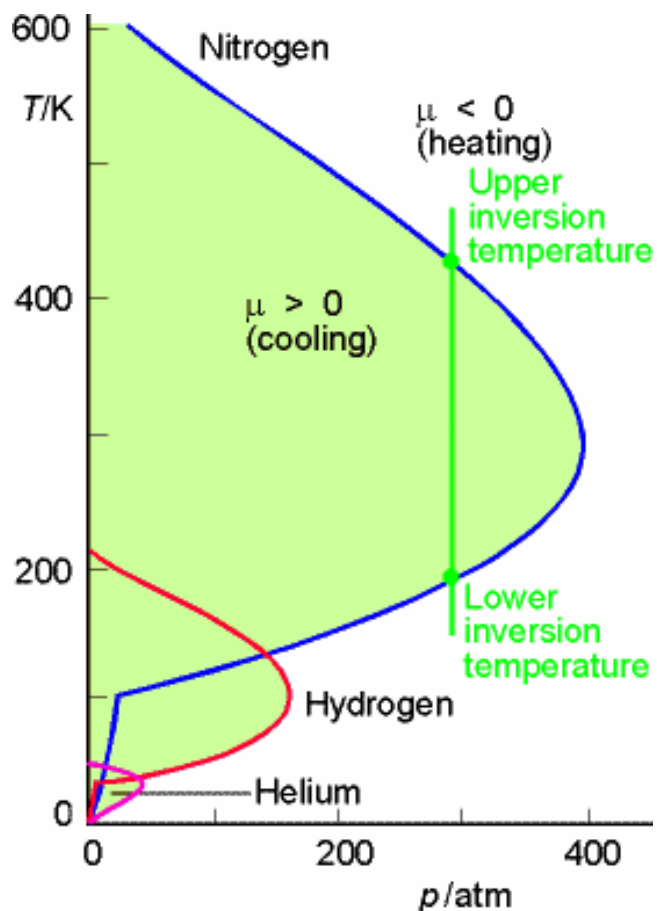


**Inside** the boundary,  $\mu > 0$  and outside it is negative. The  $T$  corresponding to the boundary at a given  $p$  is the **inversion  $T$**  of the gas at that  $p$ . Reduction of  $p$  under adiabatic conditions moves the system along one of the **isenthalps**. The inversion  $T$  curve runs through the points of the isenthalps where their slopes change from negative to positive.



## 3.2 The temperature dependence of the enthalpy

### 3). The Joule -Thomson effect: for real gases



The sign of the Joule-Thomson coefficient,  $\mu$

Gases that show a heating effect ( $\mu < 0$ ) at one  $T$  show a cooling effect ( $\mu > 0$ ) when the  $T$  is below their upper inversion temperature,  $T_I$ . A gas typically has two inversion temperatures, one at high temperature and the other at low.



## 3.3 The reaction between $C_V$ and $C_p$

We know that

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

To introduce  $H=U+pV$

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

$\alpha \pi_T V$

From the equation

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



### 3.3 The reaction between $C_V$ and $C_p$

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

$$C_p - C_V = \alpha pV + \alpha \pi_T V = \alpha (p + \pi_T) V$$

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

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





### 3.3 The reaction between $C_V$ and $C_p$

$$C_p - C_V = \alpha TV \left( \frac{\partial p}{\partial T} \right)_V \quad \leftarrow \quad \left\{ \begin{array}{l} \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \\ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \end{array} \right.$$

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



## 3.3 The reaction between $C_V$ and $C_p$

For a perfect gas

$$\alpha = \frac{1}{T} \quad \text{and} \quad \kappa_T = \frac{1}{p}$$

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

$$\underline{\underline{C_{p,m} - C_{V,m} = R}}$$



# A summary

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

1). Internal pressure,  $\pi_T$

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

For a perfect gas:  $\pi_T = 0$ .

3). Isothermal compressibility,  $\kappa_T$

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

For a perfect gas:  $\kappa_T = \frac{1}{p}$

2). Expansion coefficient,  $\alpha$

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

For a perfect gas:  $\alpha = \frac{1}{T}$

4). Joule-Thomson coefficient,  $\mu$

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

For a perfect gas:  $\mu = 0$



# Part 1: Equilibrium

1. The properties of gases
2. The First Law: the concepts
3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
6. Physical transformations of pure substances
7. Simple mixtures
8. Phase diagrams
9. Chemical equilibrium
10. Electrochemistry