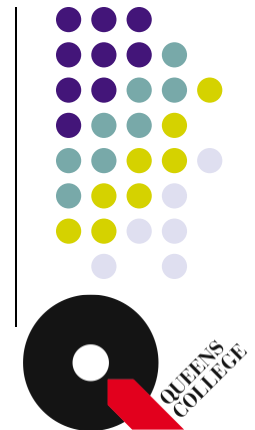


# Chap. 2. The First Law of Thermodynamics

↖ **Law of Energy Conservation**



**System** - part of the world we are interest in

**Surroundings** - region outside the system

**World or Universe** - system plus surroundings

**Open system** - transfer of matter between system and surroundings

**Closed system** - no transfer of matter

**Isolated system** - closed, no mechanical and thermal contact

Internal energy of system

(initial)

work done on system

$$\Delta U = U_f - U_i = w + q$$

Internal energy of system  
(final)



Heat transferred to system

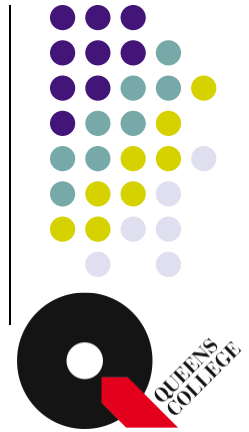
**First law holds however small the heat and work are.**

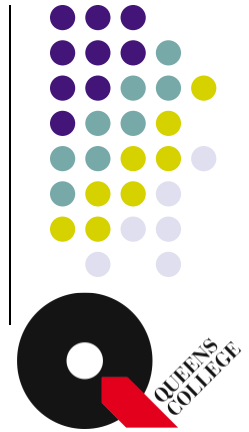
**Infinitesimal changes:**  $dU = dw + dq$

work on system due to expansion or contraction

$$dw = dw_{exp} + dw_e = -p_{ex}dV + dw_e$$

electric or other work on system





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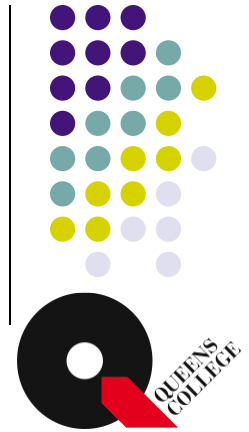
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Assume  $dw_e = 0$ .

Then,  $dU = -p_{ex}dV + dq$

**At constant volume,**  $(dU)_V = (dq)_V = C_V dT$

$C_V$  : **Heat capacity at constant volume - the amount of heat transferred to the system per unit increase of temperature**



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

**Most processes occur at constant pressure. What is the relation between heat absorbed at constant pressure and the energy?**

**Enthalpy:**  $H = U + pV$

**heat content, a state function in the unit of energy**



**The heat absorbed at constant pressure is the same as enthalpy change of the system given that its pressure is the same as the external pressure.**

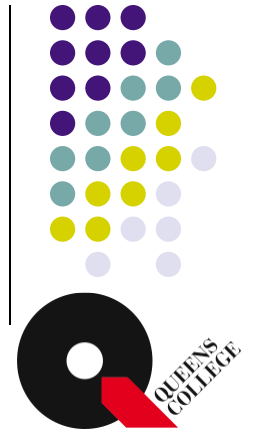
**Enthalpy:**  $H = U + pV$

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$$dH = dU + V dp + p dV = dq - p_{ex} dV + V dp + p dV$$

$$dH = dq + V dp + (p - p_{ex}) dV$$

$$\text{If } p = p_{ex}, dH = dq + V dp$$



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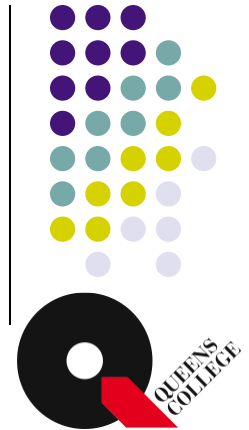
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$C_V(T)$  and  $C_p(T)$  are functions of temperature in general

### Molar Heat Capacities

$$C_{V,m}(T) = C_V(T)/n$$

$$C_{p,m}(T) = C_p(T)/n$$





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### Molar Heat Capacities

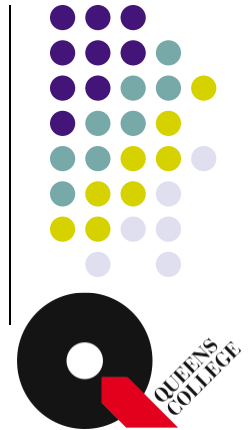
$$C_{V,m}(T) = C_V(T)/n$$

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Heat capacities can be used to determine U and H

**Molar energy** 
$$U_m(T_f) = U_m(T_i) + \int_{T_i,V}^{T_f} dT C_{V,m}(T)$$

**Molar enthalpy** 
$$H_m(T_f) = H_m(T_i) + \int_{T_i,p}^{T_f} dT C_{p,m}(T)$$



## Example, Ideal Gas

$$R = k_B N_A, k_B = 1.381 \times 10^{-23} \text{JK}^{-1}$$

$$U(T) = U(0) + \nu nRT, \nu = \frac{3}{2}, \frac{5}{2}, \text{ or } 3$$

**Monoatomic**      **Linear molecule**      **Nonlinear molecule**



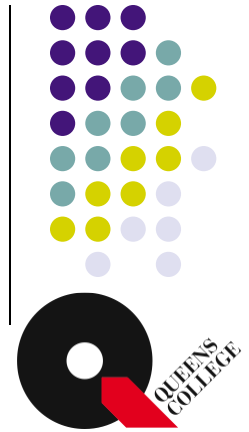
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## Example, Ideal Gas

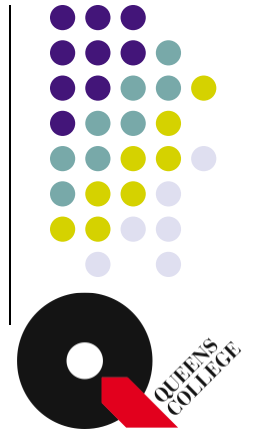
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$$C_V = \nu nR$$

$$H(T) = U(T) + pV = U(T) + nRT = H(0) + (\nu + 1)nRT$$



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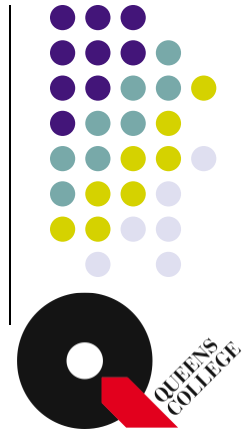
$$dU = C_V dT$$

$$w_{ad} = \Delta U = C_V (T_f - T_i)$$

$$H(T) = U(T) + pV = U(T) + nRT = H(0) + (\nu + 1)nRT$$

$$C_p = C_V + nR$$

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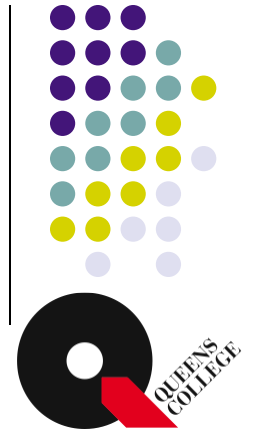
## General Relations

Consider  $U(T, V)$  as a function of T and V

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

A state function having the unit of pressure  
(named as internal pressure in Atkins)

$\pi_T = 0$  for ideal gas



## General Relations

Consider  $U(T, V)$  as a function of **T** and **V**

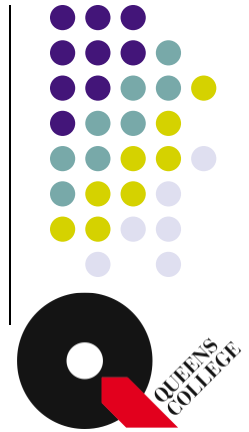
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**A state function having the unit of pressure  
(named as internal pressure in Atkins)**

Then, consider  $U(T, p)$  and  $V(T, p)$  as functions of **T** and **p**

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

**(isobaric) expansion coefficient**





## General Relations

Consider  $U(T, V)$  as a function of **T** and **V**

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

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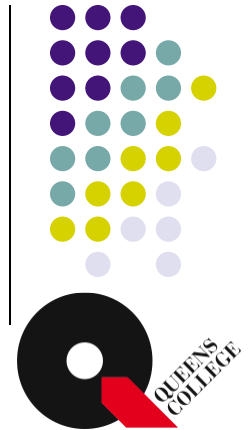
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(isobaric) expansion coefficient

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

(Note that  $H = U + pV$ )



## Another general relations

Consider temperature,  $T(H, p)$  , as a function of H and p

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



## Another general relations

Consider temperature,  $T(H, p)$  , as a function of H and p

$$dT = \left( \frac{\partial T}{\partial H} \right)_p dH + \left( \frac{\partial T}{\partial p} \right)_H dp \quad (1)$$

Take partial derivative of (1) with respect to T while H remains fixed

$$\rightarrow 1 = \left( \frac{\partial T}{\partial p} \right)_H \left( \frac{\partial p}{\partial T} \right)_H \quad (2)$$



## Another general relations

Consider temperature,  $T(H, p)$ , as a function of H and p

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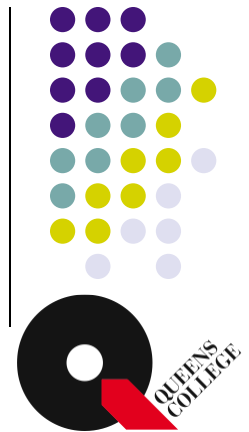
$$\Rightarrow 1 = \left( \frac{\partial T}{\partial p} \right)_H \left( \frac{\partial p}{\partial T} \right)_H \quad (2)$$

Take partial derivative of (1) with respect to H while T remains fixed

$$\Rightarrow 0 = \left( \frac{\partial T}{\partial H} \right)_p \left( \frac{\partial H}{\partial p} \right)_T + \left( \frac{\partial T}{\partial p} \right)_H$$

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

$(2)$        $\mu = \left( \frac{\partial T}{\partial p} \right)_H$       **Joule-Thompson coefficient**



## Joule-Thompson Effect - **Cooling** of gas upon **lowering** of pressure at constant enthalpy (isenthalpic process)

$$\mu > 0 \text{ for } T_{I,low} < T < T_{I,up}$$

**Consider enthalpy,  $H(T, p)$ , as a function of T and p**

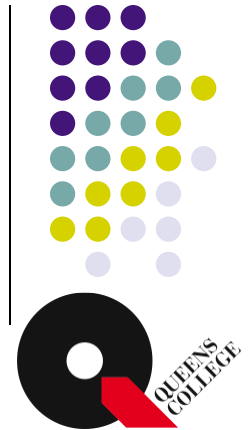
$$dH = \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial p} \right)_T dp = C_p dT - \mu C_p dp$$

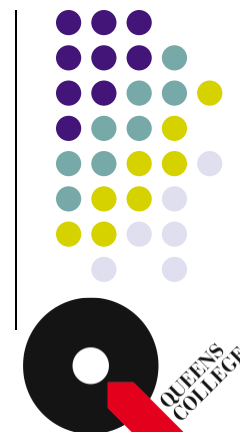
**Isothermal Joule-Thompson coefficient**

$$\mu_T = \left( \frac{\partial H}{\partial p} \right)_T = -\mu C_p$$

↑

**Easier to measure**





## Thermochemistry

Application of thermodynamics to chemical reaction.

The set of reactants and the set of products are viewed as the same system at different physical and chemical conditions.

↑  
Phase, structure, etc

↑  
Different molecules and complexes

### Standard state

Pure form at 1 bar.

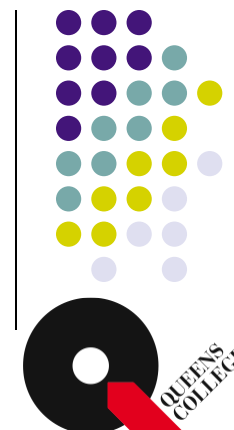
Defined at any temperature,

but refers to 298.15 K if not stated explicitly.

Standard enthalpy change  $\Delta H^\ominus$

Change in enthalpy for a process in which the initial and final states are in their standard states

See Table 2.4



## Hess' s Law

**The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.**

**Direct result of enthalpy as a state function.**

**if**  $A \rightarrow B, \Delta_{A \rightarrow B} H^\ominus$  **and**  $B \rightarrow C, \Delta_{B \rightarrow C} H^\ominus$

**then**  $\Delta_{A \rightarrow C} H^\ominus = \Delta_{A \rightarrow B} H^\ominus + \Delta_{B \rightarrow C} H^\ominus$

## Kirchhoff' s law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} dT \Delta_r C_p^\ominus \quad \text{at constant pressure}$$

Reaction heat capacity  $\Delta_r C_p^\ominus = \sum_f \nu(f) C_{p,m}^\ominus(f) - \sum_i \nu(i) C_{p,m}^\ominus(i)$

**for the chemical reaction**  $\sum_i \nu(i) M_i \rightarrow \sum_f \nu(f) M_f$