Chap. 2. **The First Law of Thermodynamics**

Law of Energy Conservation

**System** - part of the world we are interested 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

\[ \Delta U = U_f - U_i = w + q \]

- Internal energy of system (initial)
- Work done on system
- Heat transferred to system
- Internal energy of system (final)
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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**Electric or other work on system**

Assume \( dw_{\text{e}} = 0 \).

Then, \( dU = -p_{\text{ex}} dV + dq \)

**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.

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\[
dH = dU + Vdp + pdV = dq - p_exdV + Vdp + pdV
\]

\[
dH = dq + Vdp + (p - p_ex)dV
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If \( p = p_ex \), \( dH = dq + Vdp \)
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If \( p = p_{ex} \), \( dH = dq + Vdp \)

At constant pressure,

\[ (dH)_{p} = (dq)_{p} = C_{p}dT \]

**\( C_{p} \):** Heat capacity at constant pressure - the amount of heat transferred to the system per unit increase of temperature

\[ C_{p} = \left( \frac{dq}{dT} \right)_{p} = \left( \frac{\partial H}{\partial T} \right)_{p} \]
$C_V(T)$ and $C_p(T)$ are functions of temperature in general

**Molar Heat Capacities**

$$C_{V,m}(T) = \frac{C_V(T)}{n} \quad \quad \quad C_{p,m}(T) = \frac{C_p(T)}{n}$$
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**Molar Heat Capacities**

$$C_{V,m}(T) = \frac{C_V(T)}{n} \quad C_{p,m}(T) = \frac{C_p(T)}{n}$$

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

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

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

- Monoatomic
- Linear molecule
- Nonlinear molecule

↑ Monoatomic  ↑ Linear molecule
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\[ C_V = \nu nR \]
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\[ C_V = \nu n R \]

\[ H(T) = U(T) + pV = U(T) + nRT = H(0) + (\nu + 1)nRT \]
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\[ C_p = C_V + nR \]
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\[ \text{Monoatomic} \uparrow \uparrow \text{Linear molecule} \]

\[ C_V = \nu nR \quad \quad dU = C_V dT \]

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

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

\[ C_p = C_V + nR \quad \quad dH = C_p dT \]
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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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)

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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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 \( p \)

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\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

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

(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 $p$

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

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

\[ 1 = \left( \frac{\partial T}{\partial p} \right)_H \left( \frac{\partial p}{\partial T} \right)_H \]
Another general relations

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

\[
dT = \left( \frac{\partial T}{\partial H} \right)_p \; dH + \left( \frac{\partial T}{\partial p} \right)_H \; dp \tag{1}
\]

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

\[
1 = \left( \frac{\partial T}{\partial p} \right)_H \left( \frac{\partial p}{\partial T} \right)_H \tag{2}
\]

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

\[
0 = \left( \frac{\partial T}{\partial H} \right)_p \left( \frac{\partial H}{\partial p} \right)_T + \left( \frac{\partial T}{\partial p} \right)_H \tag{2}
\]

\[
\left( \frac{\partial H}{\partial p} \right)_T = -\left( \frac{\partial T}{\partial p} \right)_H \Rightarrow \; -\left( \frac{\partial T}{\partial p} \right)_H \left( \frac{\partial H}{\partial T} \right)_p = -\mu \left( \frac{\partial H}{\partial T} \right)_p \tag{2}
\]

\[
\mu = \left( \frac{\partial T}{\partial p} \right)_H \quad \text{Joule-Thompson coefficient}
\]
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.

**Standard state**

Pure form at 1 bar.

Defined at any temperature,

but refers to 298.15 K if not stated explicitly.

**Standard enthalpy change** \( \Delta H^\Theta \)

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

See Table 2.4
**Hess’ 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 \( A \rightarrow B, \Delta_{A \rightarrow B} H^\Theta \) and \( B \rightarrow C, \Delta_{B \rightarrow C} H^\Theta \)

then \( \Delta_{A \rightarrow C} H^\Theta = \Delta_{A \rightarrow B} H^\Theta + \Delta_{B \rightarrow C} H^\Theta \)

**Kirchhoff’s law**

\[ \Delta_r H^\Theta(T_2) = \Delta_r H^\Theta(T_1) + \int_{T_1}^{T_2} dT \Delta_r C_p^\Theta \]

**Reaction heat capacity**

\[ \Delta_r C_p^\Theta = \sum_f \nu(f) C_{p,m}^\Theta(f) - \sum_i \nu(i) C_{p,m}^\Theta(i) \]

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