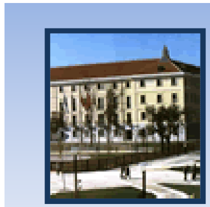
Thermochemistry



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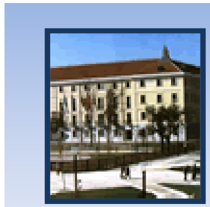


6.1. GETTING STARTED: SOME TERMINOLOGY

Thermodynamics is a branch of physics which deals with the energy and work of a system.

Thermochemistry: Thermochemistry is a branch of thermodynamics focused on the study of heat change in chemical reactions.

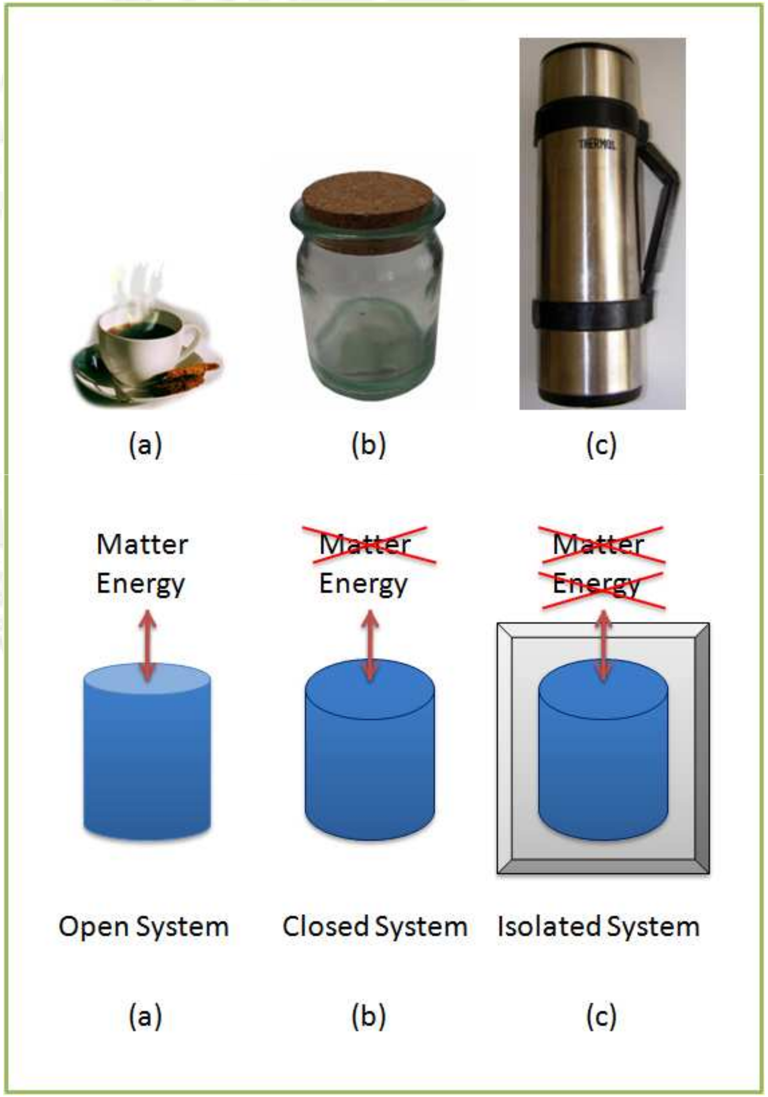
- **Heat (H)** Heat *flows* from hotter to colder bodies.
- **Work (W)** Work includes all energies but heat.

Universe = System + Surroundings

SYSTEM: **the specific part of the universe that is of interest to us.**

SURROUNDINGS: **the rest of the universe outside the system.**

- **System**
  - **Open system**
  - **Closed system**
  - **Isolated system**

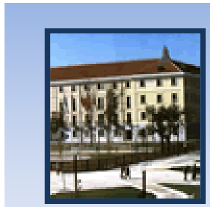


EXOTHERMIC PROCESS

- **Heat is released ($Q_f - Q_i < 0$)**
- **The reactants have more energy than the products.**

ENDOTHERMIC PROCESS

- **Heat is absorbed ($Q_f - Q_i > 0$)**
- **The products have more energy than the reactants.**



6.2. STATE FUNCTIONS

Any property that has a unique value for a specified state of a system is said to be a State Function.

$$\Delta X = X_{final} - X_{initial}$$

State function (P, V, T) ⇒ State equation

- Thermodynamic State Functions: Thermodynamic properties that are dependent on the state of the system only. (Example: ΔE and ΔH)
- Other variables will be dependent on pathway (Example: Heat (q) and Work (w)). These are NOT state functions. In these cases, the pathway from one state to the other must be defined.

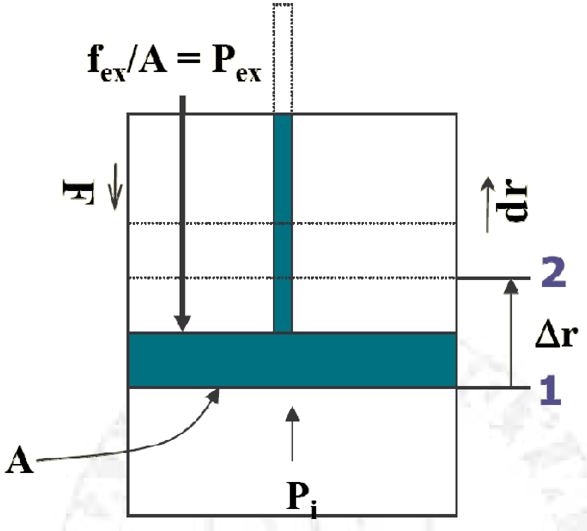
4.3. PRESSURE-VOLUME WORK

Gas expansion

$w = F \cdot r$

$F = Force$

$r = Distance$



$$w = -f_{ex}(r_2 - r_1)$$

$$w = -P_{ex} A (\Delta r)$$

$$w = -P_{ex} \Delta V$$

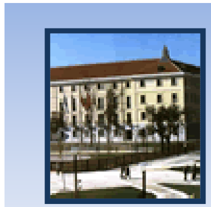
$$dw = -P_{ex} dV \qquad w = \int_{V_1}^{V_2} P_{ex} dV$$

Work is done by the system.

$$\boxed{w = p \cdot \Delta V} \Rightarrow \boxed{w = -p \cdot \Delta V}$$

HEAT ⇒ **Energy is transferred due to the different temperature of the bodies.**

(1 cal <> 4,18 J).



4.4. THE FIRST LAW OF THERMODYNAMICS

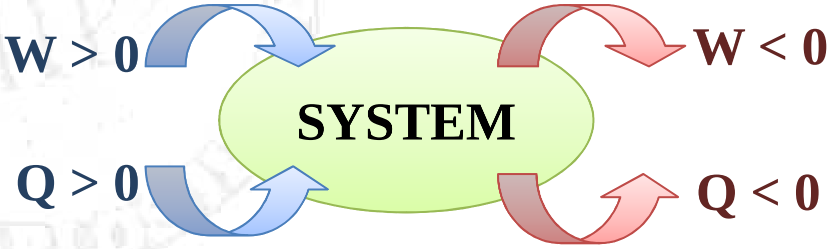
- **Law of Conservation of Energy:** **The energy of an isolated system is constant.**
  - **Internal Energy, U (E)**

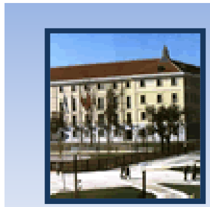
    - Total energy (potential and kinetic) in a system.

$$\Delta U_{universe} = 0$$

$$\Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0 \Rightarrow \Delta U_{system} = -\Delta U_{surroundings}$$

$$\Delta U = q + w$$





4.4. THE FIRST LAW OF THERMODYNAMICS

V = constant

$\Delta V = 0 \Rightarrow W = 0$

$\Delta U = q + w$

$\Delta U = Q_v$

P = constant

$\Delta P = 0$

$\Delta U = q + w$

$Q_p = \Delta U - w = \Delta U - (-p \cdot \Delta V)$

$\Delta H = \Delta U + \Delta(PV)$

H = State function : $\Delta H_r = H(\text{products}) - H(\text{reactants})$

- **Solids, Liquids:** $\Delta H \approx \Delta E$
- **Gases (T = constant):** $\Delta H = \Delta E + RT\Delta n$

6.5. SPECIFIC HEAT AND HEAT CAPACITY

Heat Capacity

ΔP = 0 $$C_p = \frac{dQ_p}{dT} = \frac{dH}{dT} \qquad Q_p = n\int_{T_1}^{T_2} C_p dT = nC_p\int_{T_1}^{T_2} dT = nC_p\Delta T \qquad \Delta H = nC_p\Delta T$$

ΔV = 0 $$C_v = \frac{dQ_v}{dT} = \frac{dE}{dT} \qquad Q_v = n\int_{T_1}^{T_2} C_v dT = nC_v\int_{T_1}^{T_2} dT = nC_v\Delta T \qquad \Delta E = nC_v\Delta T$$

C_v and C_p (1 mole)

$$H = E + pV \Rightarrow \frac{dH}{dT} = \frac{dE}{dT} + \frac{d(pV)}{dT}$$

$$Cp = Cv + \frac{d(pV)}{dT}$$

Solids, Liquids:

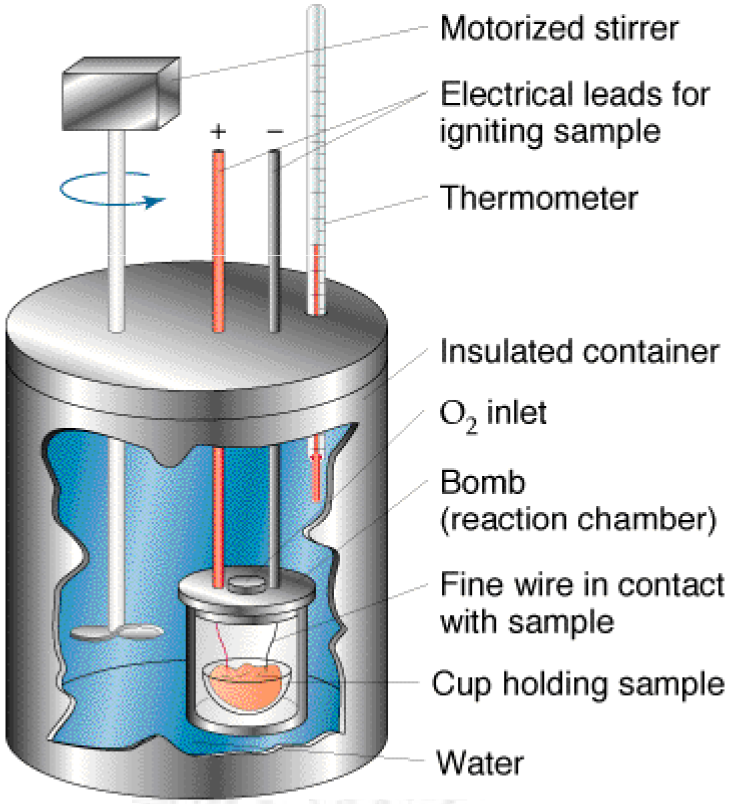
d(PV)/dT small $\Rightarrow$ $C_p \approx C_v$

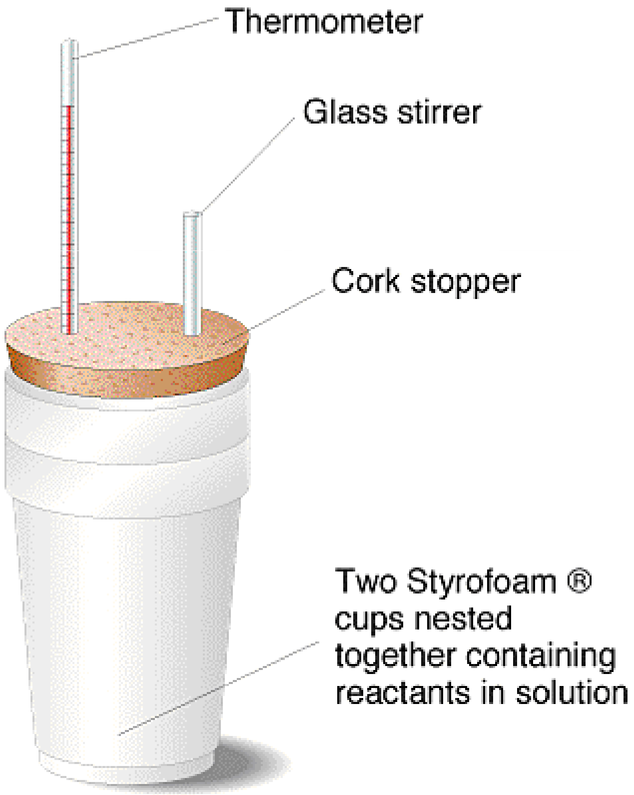
Gases:

PV = RT $\Rightarrow$ $C_p = C_v + R$

6.6. MEASUREMENT OF HEAT OF CHEMICAL REACTIONS

Calorimeter





Images from: http://www.chem.ufl.edu/~itl/2045/lectures/lec_9.html

6.7. VARIATION OF THE HEAT OF REACTIONS (ΔH & ΔE) WITH TEMPERATURE

Enthalpy

$aA + bB \rightarrow cC + dD \qquad \Delta H\left(T_2\right) = ?$

P = constant

$$\begin{tikzcd}
\mathbf{(aA + bB)\ a\ T_2} \arrow[r, "¿¿\ \Delta H_2\ ??"] & \mathbf{(cC + dD)\ a\ T_2} \arrow[d, "\Delta H''"] \\
\mathbf{(aA + bB)\ a\ T_1} \arrow[u, "\Delta H'"] \arrow[r, "\Delta H_1"] & \mathbf{(cC + dD)\ a\ T_1}
\end{tikzcd}$$

ΔH_1 is known **ΔH_2 ?**

$\Delta H_1 = \Delta H' + \Delta H_2 + \Delta H''$

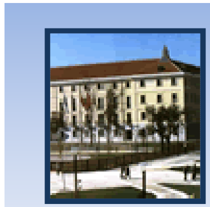
$C_p(\text{reactants}) = aC_p(A) + bC_p(B)$

$$\Delta H' = \int_{T_1}^{T_2} C_p(\text{reactants})dT$$

$C_p(\text{products}) = cC_p(C) + dC_p(D)$

$$\Delta H'' = \int_{T_2}^{T_1} C_p(\text{products})dT$$

$$\boxed{\Delta H'' = -\int_{T_1}^{T2} C_p(\text{products})dT}$$



6.7. VARIATION OF THE HEAT OF REACTIONS (ΔH & ΔE) WITH TEMPERATURE

Enthalpy

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} C_p(\text{products})dT - \int_{T_1}^{T_2} C_p(\text{reactants})dT$$

P = constant

$$\boxed{\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p dT}$$

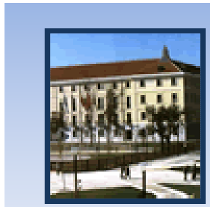
Usually ΔCp is small $\Rightarrow$ $\Delta H \neq f(T)$

Internal Energy

V = constant

$$\boxed{\Delta E_2 = \Delta E_1 + \int_{T_1}^{T_2} \Delta C_v dT}$$

Molar heat capacity at constant volumen, C_v



6.8. ENTHALPIES OF FORMATION

A) Enthalpy and Chemical Reactions

Standard Enthalpies of Formation

The enthalpy change that occurs in the formation of one mole of a substance in the standard state from the reference forms of the elements in their standard states.

The standard enthalpy of formation of a pure element in its reference state is 0.

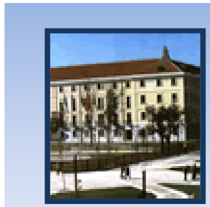
Standard Enthalpies of Reaction

For the reaction:

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^0_{rxn} = \sum n\Delta H^0_{f(products)} - \sum n\Delta H^0_{f(rea)}$$

$$\Delta H^0_{rxn} = \left[c\Delta H^0_f(C) + d\Delta H^0_f(D)\right] - \left[a\Delta H^0_f(A) + b\Delta H^0_f(B)\right]$$



6.8. ENTHALPIES OF FORMATION

B) The Indirect Determination of ΔH: Hess’s Law

The direct Method

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H_r^0 = -393{,}5\ kJ$$

$$\Delta H_r^0 = (1mol)\Delta H_f^0(CO_2, g) - \left[(1mol)\Delta H_f^0(C, graphite) + (1mol)\Delta H_f^0(O_2, g)\right]$$

$$\Delta H_r^0 = (1mol)\Delta H_f^0(CO_2, g) - [0 + 0] \quad \Rightarrow \Delta H_f^0(CO_2, g) = 0$$

The Indirect Method: Hess’s Law

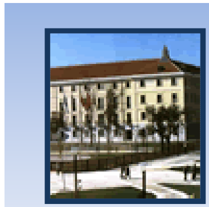
Hess's Law says that enthalpy changes are additive.

For a given reaction, ΔH is the same whether it occurs in one step or in a series of steps.

For example:

If Reaction (1) = Reaction (2) + Reaction (3)

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$



6.8. ENTHALPIES OF FORMATION

B) The Indirect Determination of ΔH: Hess's Law

Example: enthalpy of formation of acethylene

$2\ \text{C (graphite)} + \text{H}_2\ \text{(g)} \rightarrow \text{C}_2\text{H}_2\ \text{(g)}$ (non possible rxn)

$\text{C (graphite)} + \text{O}_2\ \text{(g)} \rightarrow \text{CO}_2\ \text{(g)}$ $\Delta H_r^0 = -393{,}5\ \text{kJ}$

$\text{H}_2\ \text{(g)} + \frac{1}{2}\ \text{O}_2\ \text{(g)} \rightarrow \text{H}_2\text{O (l)}$ $\Delta H_r^0 = -285{,}8\ \text{kJ}$

$2\ \text{C}_2\text{H}_2\ \text{(g)} + 5\ \text{O}_2\ \text{(g)} \rightarrow 4\ \text{CO}_2\ \text{(g)} + 2\ \text{H}_2\text{O (l)}$ $\Delta H_r^0 = -2598{,}8\text{kJ}$

$4\text{C (graphite)} + 4\text{O}_2\ \text{(g)} \rightarrow 4\text{CO}_2\ \text{(g)}$ $\Delta H_r^0 = -1574{,}0\ \text{kJ}$

$2\text{H}_2\ \text{(g)} + 2/2\text{O}_2\ \text{(g)} \rightarrow 2\text{H}_2\text{O (l)}$ $\Delta H_r^0 = -571{,}6\ \text{kJ}$

$\underline{4\ \text{CO}_2\ \text{(g)} + 2\ \text{H}_2\text{O (l)} \rightarrow 2\ \text{C}_2\text{H}_2\ \text{(g)} + 5\ \text{O}_2\ \text{(g)}}$ $\underline{\Delta H_r^0 = 2598{,}8\ \text{kJ}}$

$4\text{C (graphite)} + 2\text{H}_2\ \text{(g)} \rightarrow 2\text{C}_2\text{H}_2\ \text{(g)}$ $\Delta H_r^0 = 453{,}2\ \text{kJ}$

$2\ \text{C (graphite)} + \text{H}_2\ \text{(g)} \rightarrow \text{C}_2\text{H}_2\ \text{(g)}$ $\Delta H_r^0 = 226{,}6\ \text{kJ}$

$\Delta H_f^0\ (\text{C}_2\text{H}_2) = \Delta H_r^0\ (\text{C}_2\text{H}_2)/\text{mol} = 226{,}6\ \text{kJ/mol}$

6.9. THE SECOND LAW OF THERMODYNAMICS: ENTROPY.

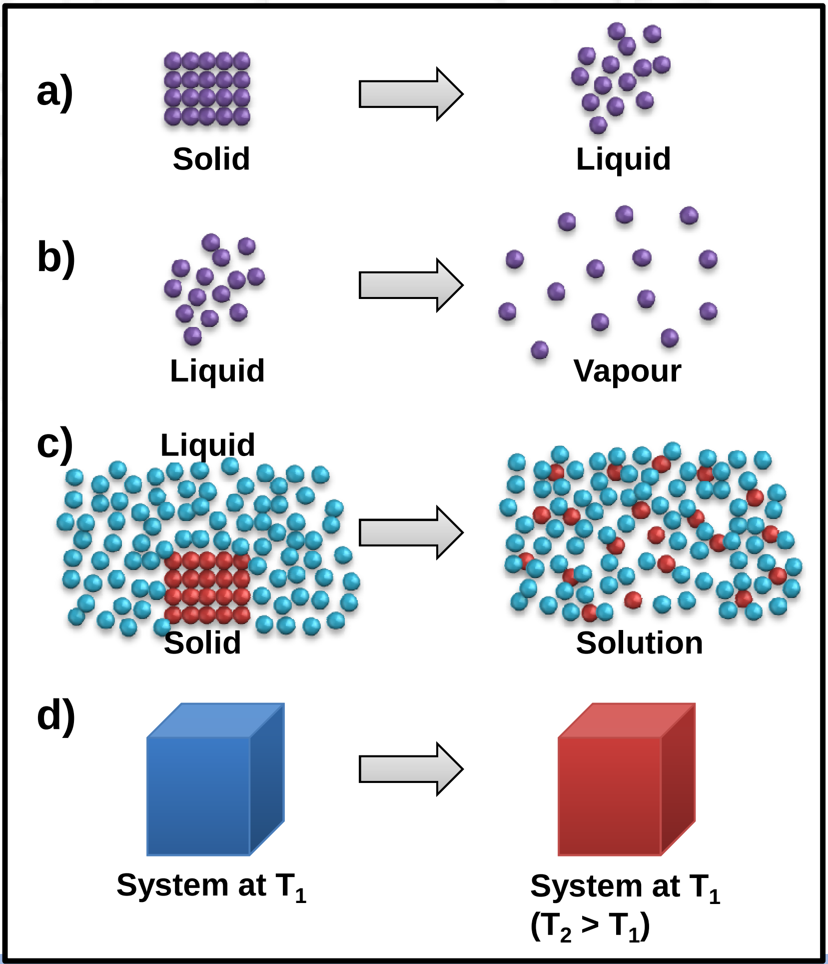
It is a measure of the randomness of molecules in a system.

Entropy is a state function:

$$\Delta S = S_{final} - S_{initial}$$

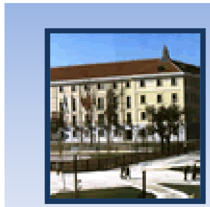
Examples:

a) Melting of a solid
b) Vaporization of a liquid
c) Solution formation
d) Increase of the temperature of a body



In every case

$$\Delta S = S_{final} - S_{initial} > 0$$



6.9. THE SECOND LAW OF THERMODYNAMICS: ENTROPY.

▪The Second Law of Thermodynamics

$$\Delta S_{total} = \Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$ **Spontaneous Process**

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$$ **Equilibrium**

All spontaneous processes produce an increase in the entropy of the universe.

▪Evaluating entropy changes

Given the reaction: $aA + bB \rightarrow cC + dD$

Like "H", the entropy is a state function and so the standard entropy of a chemical reaction can be calculated as follows:

$$\Delta S_{system} = \Delta S^0_{reaction} = \left[cS^0_C + dS^0_D\right] - \left[aS^0_A + bS^0_B\right]$$

$$\Delta S^0_{reaction} = \sum nS^0_{products} - \sum mS^0_{reactants}$$

General Chemistry

▪Evaluating entropy changes

P = constant $\Delta S_{surroundings} \propto -\Delta H_{system}$

Exothermic Process $\Delta H_{system} < 0 \Rightarrow \Delta S_{surroundings} > 0$

Endothermic Process $\Delta H_{system} > 0 \Rightarrow \Delta S_{surroundings} < 0$

$$\boxed{\Delta S_{surroundings} = -\frac{\Delta H_{system}}{T}}$$

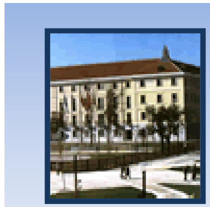
▪Spontaneous processes. Reversibility and Spontaneity.

Reversible Processes ⇒ **quasistatic processes**

Reversible Expanssion and compression: ($P_{int} = P_{ex} \pm dP$)

Reversible change of temperature: ($T_{ex} = T_{int} \pm dT$)

Irreversible Processes ⇒ **the changes in the system are finite**



▪Reversible and irreversible processes

$W_{reversible} < W_{irreversible}$

Reversible Compression $(P_{int} = P_{ex} - dP)$:

$$W_{rev} = -\int P_{ex}\, dV = -\int (P_{int} + dP)\, dV \approx -\int P_{int}\, dV$$

Irreversible Compression $(Pex > P_{int})$:

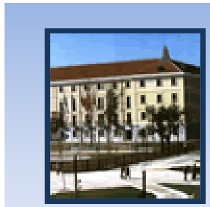
$$w_{irrev} = -\int_{V_1}^{V_2} P_{ex} dV > -\int_{V_1}^{V_2} P_{int} dV = w_{rev}$$

Reversible Compression of an Ideal Gas:

$$W_{rev} = -\int P_{int}\, dV; \qquad (P_{int} = nRT/V)$$

$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT\ln\frac{V_2}{V_1}$$

$$w_{irrev} = -\int_{V_1}^{V_2} P_{ex} dV = -P_2(V_2 - V_1) > 0$$



▪Reversible and irreversible processes

$Q_{rev} > Q_{irrev}$

$Q_{rev} = \Delta E - w_{rev}$
$Q_{irrev} = \Delta E - w_{irrev}$

$Q_{rev} - Q_{irrev} = w_{irrev} - w_{rev}$
si $w_{reversible} < w_{irreversible} \Rightarrow Q_{rev} > Q_{irrev}$

Calculating Entropy

$$\Delta S \equiv \int_1^2 \frac{\delta Q_{rev}}{T}$$

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

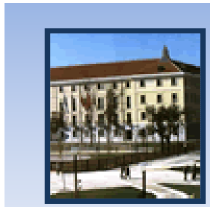
For an Ideal Gas, according to the kinetic theory: $E_c = 3/2RT$
If $T = \text{constant} \Rightarrow E = \text{constant} \Rightarrow \Delta E = 0 \Rightarrow w + Q = 0 \Rightarrow Q = -w$

$$Q_{rev} = -w_{rev} = nRT \ln V_1/V_2$$

$$\Delta S = Q_{rev}/T = nR \ln V_2/V_1$$

For an expanssion: $V_2 > V_1 \Rightarrow \Delta S > 0$

Irreversible isothermal Expanssion: $\Delta S_{gas} = nR \ln V_2/V_1$ **(S state function)**



6.10. ENTROPY AND THE THIRD LAW OF THERMODYNAMICS

▪The Third Law of Thermodynamics

The entropy of a pure perfect crystal at 0 K is zero.

S_i = Initial Entropy
S_f = Final Entropy

$$\Delta S = S_f - S_i$$

S_i = entropy at 0 K

$$\Delta S = S_f$$

The entropy of a certain substance increases with temperature

For one mole:

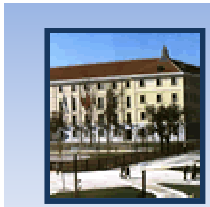
$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT \Rightarrow S_T - S_0 = \int_0^T \frac{C_p}{T} dT$$

Since $S_0 = 0$ $\Rightarrow$

$$S_T = \int_0^T \frac{C_p}{T} dT$$

S^0_{298} for a substance that melts at $T_f < 298$ K

$$\Delta S^0_{298} = \int_0^{T_f} \frac{C_p}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{298} \frac{C_p'}{T} dT$$



6.11. SPONTANEOUS CHANGE: FREE ENERGY

According to the second law of thermodynamics, for an spontaneous process:

$\Delta S = 0 \Rightarrow$ Reversible Process
$\Delta S > 0 \Rightarrow$ Irreversible or Spontaneous Process

$\Delta S_{surroundings}$ is difficult to calculate, therefore:

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surround} > 0;$$
$$\Delta S_{univ} = \Delta S_{syst} - \Delta H_{syst}/T > 0;$$
$$T\cdot\Delta S_{univ} = T\cdot\Delta S_{syst} - \Delta H_{syst} > 0;$$

Gibbs Free Energy $G = H - T\cdot S$ $\quad$ **$\Delta G = \Delta H - T\cdot\Delta S$**

Since G is a state function ⇒ $\Delta G^0_{reaction} = \Delta G^0_{products} - \Delta G^0_{reactants}$

$\Delta G < 0$	**Spontaneous Process**	
$\Delta G = 0$	**Equilibrium is established**	**Criteria for spontaneous changes**
$\Delta G > 0$	**Non-Spontaneous Process**	

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