

Chapter (2)

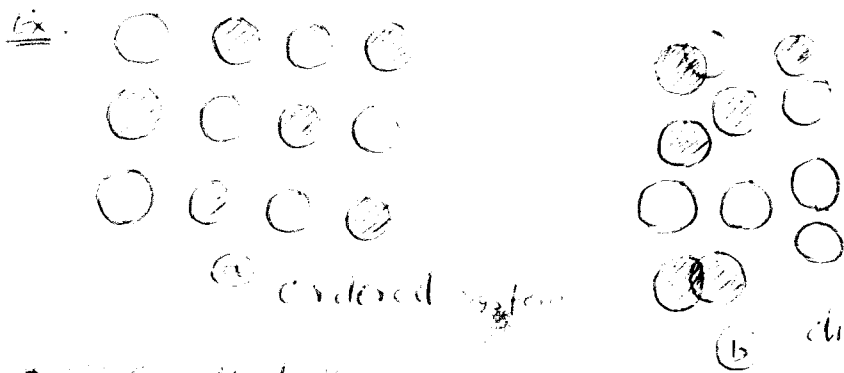
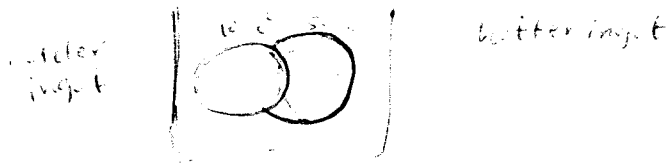
Entropy, Free Energy and Chemical Equilibrium

The facts which are both statements of the second law of thermodynamics

- ① heat always flows from a hotter to a colder body - never in the reverse direction.
- ② an isolated system always tends to take up a more disordered ~~form~~ form never of its own accord becoming more ordered.

Ex if two ingots one at 100°C and the other at 20°C were placed closed to one another in an insulating pit with no other source of heat.

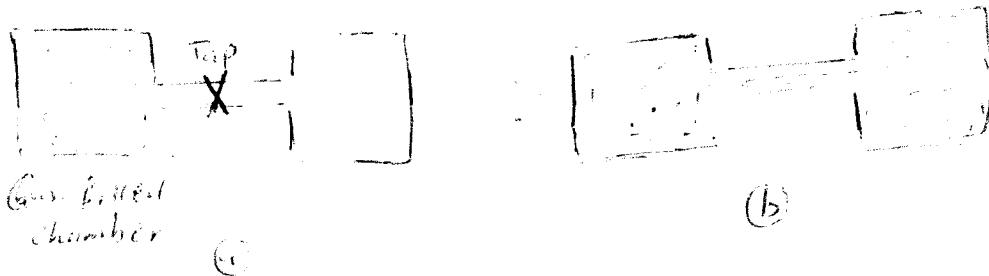
* The temperature of the hotter ingot would always decrease as heat flowed out from it (by radiation, convection or conduction) to raise the temperature of the colder ingot.



- * we say that the counters in (a) are more ordered than those in (b)
- * The state (b) is more probable than state (a) and can calculate by the techniques of statistics the "probability" W of the two systems

$$W(b) > W(a) \quad (\text{A more disordered system is more probable than more ordered system}).$$

Ex: The ~~states~~ molecules of a gas enclosed in a chamber which is connected by a tap. If the tap is opened the gas molecules, by their random motion in the space, will enter the second chamber until on the average there will be the same number of molecules in each chamber.



* Condition (b) is more probable than condition (a) and is more disordered than condition (a).

* A "spontaneous change" has taken place, accompanied, as always, by an increase in probability and therefore an increase in the disorder of the system.

The Statistical Nature of the Second Law of Thermodynamics

~~Second Law of Thermodynamics~~: Thermodynamics is not concerned with the behaviour of the individual ~~part~~ molecules of a gas system - only the statistical average behaviour of the system.

* The pressure exerted by gas is the resultant of the distribution of forces produced by the motion and collision of many molecules - each with its own individual energy and in considering the pressure of a gas we do not watch the effect of each individual molecule only that of the motion of all the molecules.

* In addition to an energy change, we can therefore have a change in the state of order accompanying a chemical or physical change in a system, and this change in the state of order can be expressed as a change in a property of the system, the entropy (S) which is related with the thermodynamic probability (w) as:

$$S = k \ln W + S_0$$

where

S is the entropy of the system, k is the Boltzmann constant (measures constant R , divided by Avogadro number, $k = R/N_A$ the gas constant per single molecule).

w is the thermodynamic probability of the system, S_0 is a constant, the entropy when w is unity.

~~Entropy of a system is a measure of the amount of disorder in the system.~~

* The thermodynamic probability of the system, w , is defined as the ratio of the probability of the existing state of the system to the probability of the state of complete order in the system for the same energy and volume.

* The Third Law of Thermodynamics is concerned with the value of S_0 , that a perfect crystalline solid should be completely ordered at the absolute zero of temperature and should therefore have zero entropy.

* The Third Law assumes this, giving S_0 the value of zero because in a condition of perfect order, $w=1$ and $S = S_0 = 0 \Rightarrow$ Thus we have

$S = k \ln \Omega$ from this relationship we see that as the system becomes

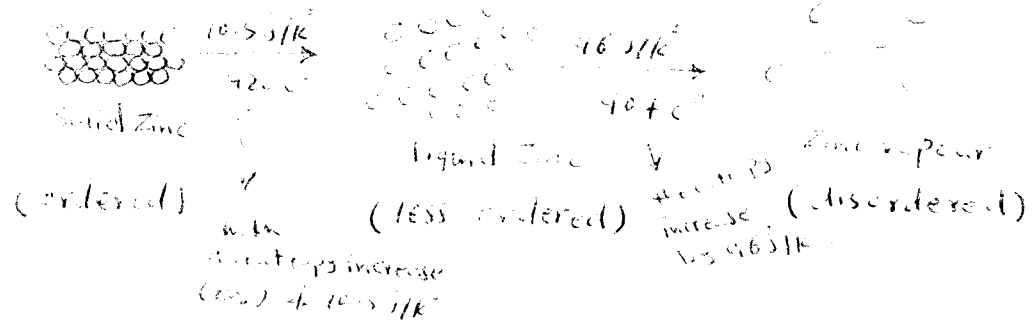
more disordered, Ω increases and S increases. \checkmark

* The entropy of the system can be used as measure of the state of order or probability of the system.

* The second law of Thermodynamics; ~~as~~ a spontaneous process is always accompanied by an increase in the total entropy of the system and its surroundings.

* The hot object will have higher entropy than ~~the~~ ~~the~~ the cold object, when heat flows from the hot object to the cold object the entropy of the cold object will increase and that of the hot object will decrease, this continues until both objects are at the same temperature and we reach equilibrium - the state of the maximum entropy. (It must be remembered

that the entropy of the system and its ~~surroundings~~ surroundings will increase)

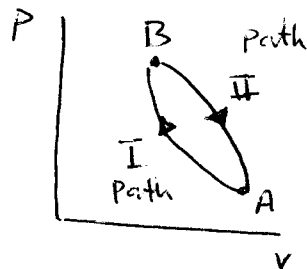


Cyclic processes and Entropy

Figure shows a cycle in which the system is changed from A to B and back again even though by two different paths I and II. From the First law of Thermodynamics and the nature of thermodynamic variables, the change in internal energy ΔU will be Zero.

$$\Delta U = q - W$$

$\therefore q = W$ as $\Delta U = 0$ (The work done by the system must be the same as the heat absorbed by the system q)



* For heat engine which can convert heat into mechanical work (e.g. a steam engine) we can define the efficiency of the ~~heat~~ machine as the fraction of heat absorbed by the machine which can be converted into work.

* ~~Carot's~~ Carnot's Cycle ^{Theorem or Theory (1824)} which stated that all machines working thermodynamically reversibly in cycles between the same temperatures of source and sink have the same efficiency.

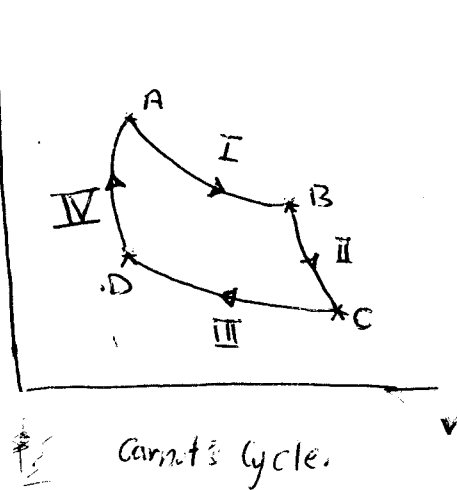
* Simple Machine, in which the working substance is 1 mole of a perfect gas contained in a cylinder with a frictionless, weightless piston. The cycle is shown in Fig. where A is the starting point and it is carried out as follows:

A) Stage I, The gas at temperature T_1 , pressure P_A and volume V_A is allowed to expand isothermally and reversibly to B where its pressure is P_B & volume V_B . The work done by the gas is

$$W_I = RT_1 \ln \frac{V_B}{V_A} = q_I, \text{ the heat absorbed by the gas.}$$

$$\Delta U_I = 0; q_I = W_I$$

$$W_I = RT_1 \ln \frac{P_A}{P_B}$$



Stage II: The gas is then expanded adiabatically (with no heat exchange with its surroundings) to C

تدرج هذا التمدد وهو يوصف بالانتفاخية في درجته كمرارة T_2 في
 لا يوجد تبادل للحرارة مع الوسط المحيط، والغاز يبرد أثناء التمدد
 وتنتج الشغل من خلال انخفاض الطاقة الحركية للجزيئات
 والحرارة تنتج من خلال انخفاض الطاقة الحركية للجزيئات

$q = 0$; volume V_C , pressure P_C , temperature T_2

because the work done is at the expense of a fall in kinetic energy of the gas molecules. The energy produced when a gas cools under these conditions is related to the molar heat capacity at constant volume C_V as follows:

$$W_{II} = C_V (T_1 - T_2) \Leftrightarrow \Delta U_{II} = -W_{II} = C_V (T_2 - T_1)$$

Stage III: The gas is compressed isothermally to D the work done by the gas is,

$$W_{III} = RT_2 \ln \frac{V_D}{V_C} = q_{III}$$

$$W_{III} = RT_2 \ln \frac{P_C}{P_D}$$

$$(\Delta U_{III} = 0, q_{III} = W_{III})$$

Stage IV: To complete the cycle, the gas is compressed adiabatically to A and the work done by the gas is

$$T_1, P_A, V_A \quad q_{IV} = 0$$

$$\Delta U_{IV} = -W_{IV} = C_V (T_1 - T_2)$$

$$W_{IV} = C_V (T_2 - T_1) \quad * \swarrow$$

Therefore the total work done by the gas in completing the cycle is

$$W = W_I + W_{II} + W_{III} + W_{IV}$$

$$W = RT_1 \ln \frac{V_B}{V_A} + C_V (T_1 - T_2) + RT_2 \ln \frac{V_D}{V_C} + C_V (T_2 - T_1)$$

$$= RT_1 \ln \frac{V_B}{V_A} + RT_2 \ln \frac{V_D}{V_C}$$

$$= q_{I+III} \text{ the net heat absorbed by the system.}$$

For an adiabatic expansion, between Temperature T_1 and T_2 it is known that if V_1 is the volume at T_1 and V_2 the volume at T_2 .

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \quad \text{where } \gamma = c_p/c_v$$

stages II and IV are adiabatic expansions between the same temperature T_1 and T_2 , so that

$$\frac{T_1}{T_2} = \left(\frac{V_D}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_B}\right)^{\gamma-1}$$

Therefore $\frac{V_D}{V_A} = \frac{V_C}{V_B}$ and $\frac{V_D}{V_C} = \frac{V_A}{V_B}$

$$W_T = R T_1 \ln \frac{V_B}{V_A} + R T_2 \ln \frac{V_A}{V_B}$$

$$= R(T_1 - T_2) \ln \frac{V_B}{V_A}$$

Hence

Efficiency of the heat engine = $\frac{W_T}{Q_I} = \frac{R(T_1 - T_2) \ln \left(\frac{V_B}{V_A}\right)}{R T_1 \ln \left(\frac{V_B}{V_A}\right)}$

$$= \frac{T_1 - T_2}{T_1}$$

Thus the efficiency of all reversible heat engine is only related to the temperature of source and sink (T_1 and T_2 respectively) and is independent of the nature of the working substance.

* note here that no heat engine can be 100% efficient.

* From the examination of Carnot's cycle we see that

$$\frac{W}{Q} = \frac{T_1 - T_2}{T_1}$$

and $W = Q_I + Q_{III} \Rightarrow \frac{Q_I + Q_{III}}{Q_I} = \frac{T_1 - T_2}{T_1}$

$$1 + \frac{Q_{III}}{Q_I} = 1 - \frac{T_2}{T_1} \Rightarrow \frac{Q_{II}}{T_1} = -\frac{Q_{III}}{T_2} \quad \text{and} \quad \frac{Q_I}{T_1} + \frac{Q_{III}}{T_2} = 0$$

we can say in general, that $\sum \frac{q}{T} = 0$ for any reversible cycle.

(*) Clausius called this ratio of the heat absorbed by a system, q , to the temperature at which it is absorbed, T , the entropy change of the system. where an infinitesimal change in entropy ds is defined by the relationship $ds = \frac{dq}{T} = \frac{dq_{rev}}{T}$

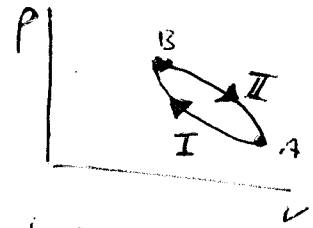
Entropy was later found to bear a relationship to the probability of a system $\Rightarrow S = k \ln W$

Entropy is an extensive property of the system as it depends on the mass of the system, and is a thermodynamic variable depending only on the state of the system not on its history. Its dimensions are those of energy divided by temperature and the usual unit is joules per degree kelvin per mol. $\frac{J/mol}{K} = J/mol \cdot K$

- * As the system absorbs heat energy, its entropy will increase.
- * The second law of thermodynamics in the (efficiency); No practical heat engine can have 100% efficiency, and heat energy cannot be completely transformed into mechanical energy.

Some Thermodynamic Relationships Involving Entropy

A) The entropy of the system A, S_A
 $\uparrow \quad \rightarrow \quad \leftarrow \quad \downarrow$
 B, S_B



So that if the system changes reversibly from state A to state B

$$\Delta S_{A \rightarrow B} = S_B - S_A \quad ; \quad \Delta S_{B \rightarrow A} = S_A - S_B$$

If the change were irreversible, ΔS would still be the same because S is a thermodynamic variable. In completing the cycle $A \rightarrow B \rightarrow A$

$$\Delta S = S_B - S_A + S_A - S_B = 0 \quad (\text{because we finish up where we started}) \text{ and there is no net change in entropy.}$$

- * If the change is adiabatic, no heat is absorbed or evolved, ΔS is zero and the change is isentropic.

* To calculate the change in entropy (ΔS)

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{\delta q}{T} \quad (\text{where } S_2 \text{ and } S_1 \text{ are the entropy of the system at temperature } T_2 \text{ and } T_1 \text{ respectively}).$$

at constant pressure $\Rightarrow C_p = \frac{\delta q_p}{dT}$

$$\text{Therefore } ds = \frac{\delta q_p}{T} = \frac{C_p dT}{T} \Rightarrow \Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{\delta q_p}{T} = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

Similarly, at constant volume

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v dT}{T}$$

If the pressure and volume are not constant for a small heat change -

$$dq = dU + pdv$$

$$= C_v dT + pdv$$

Therefore $ds = \frac{dq}{T} = C_v \frac{dT}{T} + \frac{pdv}{T} = C_v \frac{dT}{T} + R \frac{dv}{v}$???

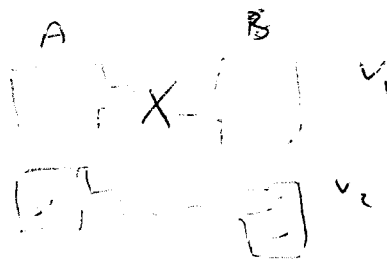
because $PV = RT$ for an ideal gas

There fore $\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} C_v \frac{dT}{T} + \int_{v_1}^{v_2} R \frac{dv}{v}$

* for an isothermal process, T is constant and

$$\Delta S = \int_{v_1}^{v_2} \frac{R dv}{v} = R \ln \frac{v_2}{v_1}$$

Ⓟ for ex. isothermal process



$$\left. \begin{matrix} v_A = v_1 \\ v_B = 2v_1 \end{matrix} \right\} \frac{v_2}{v_1} = 2$$

$$\Delta S = R \ln 2 = 8.314 \times 0.6931$$

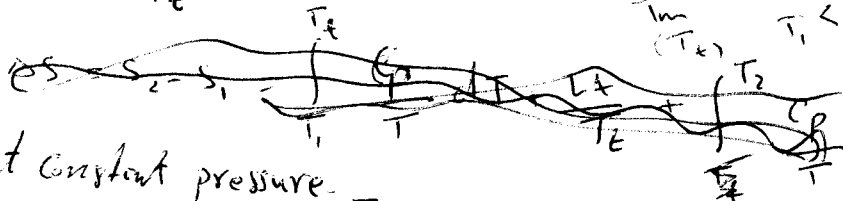
$$= 5.762 \text{ J/K-mol}$$

Process (R = 8.314 J/mol.K)
R?

ⓐ If a phase transformation occurs in the Temperature range, there will be an entropy change accompanying that transformation equal to the heat transformation (L_t) divided by the transformation temperature T_t

$$\Delta S_t = \frac{L_t}{T_t}$$

solid $[T_1]$ x liquid $[T_2]$
 $T_m (T_t)$ $T_1 < T_m < T_2$
 (T_t)



at constant pressure.

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_t} \frac{C_p}{T} dT + \frac{L_t}{T_t} + \int_{T_t}^{T_2} \frac{C_p}{T} dT$$

* C_p ~~constant~~ constant for short temperature range.

* $C_p = a + bT + cT^{-2}$ for large temperature range.

* Standard entropies of substance are tabulated - that is the entropy at (298K) ^{25°C}
Here $\Rightarrow \Delta S = S_{298} - S_0 \Rightarrow S_0 = 0$ the entropy of substance at 0°C, is zero.

Ex calculate the entropy of Zinc at 727°C

$$S_{298} = 41.63 \text{ J/K mol.}$$

$$L_f = 7280 \text{ J/mol at } 420^\circ\text{C}$$

$$\text{Solid Zinc, } C_{p(s)} = 22.38 + 10.04 \times 10^{-3} T \text{ J/mol}$$

$$\text{Liquid Zinc, } C_{p(l)} = 31.38 \text{ J/mol}$$

Ans.

$$\Delta S = \int_{298}^{693} \frac{C_{p(s)}}{T} dT + \frac{L_f}{T_f} + \int_{693}^{1000} \frac{C_{p(l)}}{T} dT$$

$$S_{1000} - S_{298} = \int_{298}^{693} \left(\frac{22.38}{T} + 10.04 \times 10^{-3} \right) dT + \frac{7280}{693} + \int_{693}^{1000} \frac{31.38}{T} dT$$

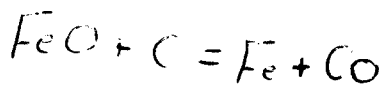
$$= \left[22.38 \ln T + 10.04 \times 10^{-3} T \right]_{298}^{693} + 10.50 + \left[31.38 \ln T \right]_{693}^{1000}$$

$$= 22.89 + 10.50 + 11.46$$

$$S_{1000} - 41.63 = 44.85 \Rightarrow S_{1000} = 44.85 + 41.63 = 86.48 \text{ J/K mol}$$

Imp

Entropy is an extensive property of the system so that entropy values are additive in the same way as heat contents, the entropy change for a reaction is obtained by summation of the entropies of reactants and products, for example ~~at~~ in the reaction.



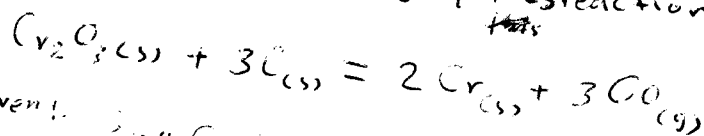
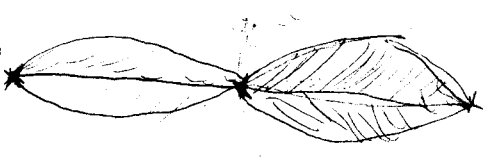
$$\Delta S = S_{\text{Fe}} + S_{\text{CO}} - S_{\text{FeO}} - S_{\text{C}}$$

$$= \sum \text{products} - \sum \text{reactants}$$

(2) Spontaneous change takes place in a system when the total entropy change of the system and its surroundings is positive.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0, \Delta S = 0 \text{ (irreversible)}$$

Ex calculate the entropy of the reaction at 25°C



Given:

$$S_{298} \text{Cr}_2\text{O}_3(s) = 19.4 \text{ cal/deg/mol}; S_{298} \text{Cr}(s) = 5.68 \text{ cal/deg/mol}$$

$$S_{298} \text{C}(s) = 1.36 \text{ cal/deg/mol}; S_{298} \text{CO}(g) = 47.3 \text{ cal/deg/mol}$$

$$\Delta S_{298} = 2S_{298} \text{Cr}(s) + 3S_{298} \text{CO}(g) - S_{298} \text{Cr}_2\text{O}_3(s) - 3S_{298} \text{C}(s)$$

$$\Delta S_{298} = (2 \times 5.68) + (3 \times 47.3) - 19.4 - (3 \times 1.36)$$

$$= 129.78 \text{ cal/deg}$$

(9)

(*) when a spontaneous change takes place in a system, the second law of thermodynamics states that the total entropy change of the system and its surroundings is positive.

Ex: ~~two~~ two ingots of the same weight of iron at temperature of 400°C and 200°C respectively, assuming any heat transfer considered must be exclusively between the two ingots. Given ($C_p = 17.49 + 24.77 \times 10^{-3} T \text{ J/K}\cdot\text{mol}$)

If heat is transferred from the hot to the cold ingot until the temperature of the two ingots is the same (300°C). The entropy change accompanying this process can be calculated by:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT = \int_{T_1}^{T_2} \left(\frac{17.49}{T} + 24.77 \times 10^{-3} \right) dT$$

For the hot ingot

$$\Delta S_H = \int_{473}^{373} \left(\frac{17.49}{T} + 24.77 \times 10^{-3} \right) dT = -5.289 \text{ J/K}\cdot\text{mol}$$

for the cold ingot

$$\Delta S_C = \int_{273}^{373} \left(\frac{17.49}{T} + 24.77 \times 10^{-3} \right) dT = +5.832 \text{ J/K}\cdot\text{mol}$$

The total entropy change of the system and its surroundings is given by

$$\Delta S_H + \Delta S_C = +0.544 \text{ J/K}\cdot\text{mol}$$

This is positive, so that the process is spontaneous according to the second law of thermodynamics.

if the hot ingot were to gain heat from the cold ingot so that its temperature rose from 400 to 600°C , while the temperature of cold ingot dropped from 200 to 0°C .

$$\Delta S_H + \Delta S_C = +9.48 - 14.52 = -5.04 \text{ J/K}\cdot\text{mol}$$

This is negative and the process is not spontaneous.

(Heat will not flow from a colder to a hotter body).

