T.D.C Part II

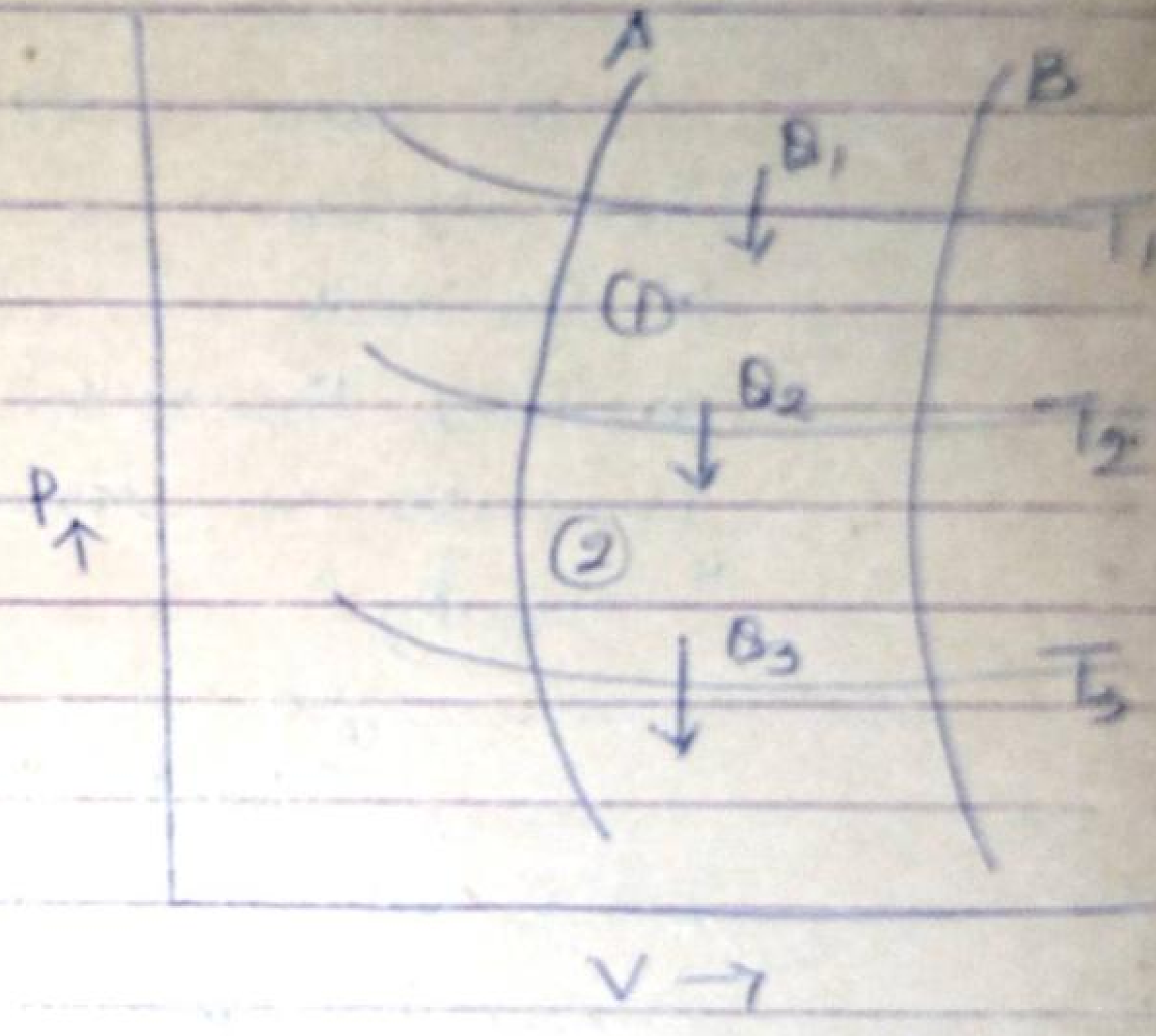
Chemistry (Hons) : Paper IV
Physical Chemistry (Gr. A)

Thermodynamics

Entropy →

Clausius first introduced a new thermodynamical function called entropy and restated the second law in terms of it. Entropy is a real physical entity like press. and temp. but can not be felt like them. It defines adequately the thermodynamical state of any working substance. More important than this is that it differentiates two adiabatics as temp. differentiates two isothermals. It is the single valued function of state and hence, independent of how the state is reached. The change in entropy of a body depends only on the initial and final states and nothing else.

The figure shows three isothermals crossed by two adiabatics A, B. We get two carnot cycles marked by (1) and (2). According to the carnot's principle



$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

where, Q_1 = heat absorbed at T_1

Q_2 = heat rejected at T_2

similarly,

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$$

Hence,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \text{constant } (K).$$

Thus, in passing from one adiabatic to another by either absorption or rejection of hea[t] Q/T remains constant. This constant ratio is knas the change of entropy between the two states corresponding to two adiabatics. If the adiabatics lie infinitely close to each other, then the change of entropy between the two states is given by

$$dS = \frac{dQ}{T} \rightarrow \text{Mathematical formulation of 2nd law.}$$

In general, the change of entropy in passing from adiabatic A to B corresponding to entropies S_1 and S_2 is

$$\int_{S_1}^{S_2} dS = S_2 - S_2 = \int_A^B \frac{dQ}{T}$$

The above expression is ~~the~~ function of the thermodynamic co-ordinates of a system and refers to the value of the function at the final state minus the value at the initial state. This function is denoted by S and is called the "entropy."

"That thermal ~~properties~~ property of a body which remains constant during an adiabat reversible process, when no heat is added or to or removed from it is called entropy."

Properties →

(i) Entropy is a real physical entity like pressure and temp. but can not be felt like them. It defines adequately the thermodynamical state of any working substance.

(ii) It differentiates two adiabatics as temp. differentiates two isothermals. For an adiabatic process $dQ = 0$, and so $dQ = 0$, which shows that entropy remains constant during an adiabatic reversible process. Thats why the adiabatics on the P-V diagram are called "isentropics"

(iii) The entropy is a single valued function of the thermodynamic co-ordinates defining the state of the system, viz pressure, temp., vol., internal energy and its change between the two states is equal to the integral of the quantity dQ/T between the states along any reversible path joining them. dS is an exact differential.

(iv) In a reversible process, the change of entropy is zero, i.e $\oint \frac{dQ}{T} = 0$. This is clausius theorem.

(v) The entropy of an isolated system can't decrease. either it remains constant (reversible process) or increases (irreversible process)

(vi) From the first law of thermodynamics

$dQ = dU + pdv$

$\therefore dS = \frac{dQ}{T} = \frac{dU + pdv}{T}$

From this equation we see that entropy is extensive property. It is proportional to the mass of the substance taken. for if we take n1 gm of the substance, [redacted] $dU = n_1 du$ and $dv = n_1 dv$. and so, $dS = n_1 ds$

(vii) Absorption of heat (+L) causes increase in entropy and vice-versa.

(viii) ΔS is completed through a reversible path.

(ix) ΔS is expressed in cal degree^{-1}

1 cal deg^{-1} mole^{-1} is known as one entropic unit (e.u)