

Gibbs Free Energy with Pressure and temperature

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Gibbs free energy G , combines enthalpy and entropy into a single value. The change in free energy ΔG is equal to the sum of enthalpy plus the product of the temperature and entropy of the system, ΔG can predict the direction of the chemical reaction under two conditions:-

- 1) Constant temperature
- 2) Constant pressure.

If ΔG is positive then the reaction is nonspontaneous (i.e. an the input of external energy is necessary for the reaction to occur - and if it is negative then it is spontaneous (occurs without external energy input))

Introduction \rightarrow

Gibbs energy was developed in 1870s.

He originally termed this energy as the 'available energy' in a system. This quantity is the energy associated

with a chemical reaction that can be used to do work and is the sum of the enthalpy (H) and the product of the temperature and the entropy (S) of the system. This quantity is defined as follows:-

$$G = H - TS \quad \text{--- (I) } \quad \text{where } H = U + PV$$

or more completely as

$$G = U + PV - TS \quad \text{--- (II)}$$

where $U =$ Internal Energy

$P =$ Pressure

$V =$ Volume

$T =$ Temperature

$S =$ Entropy

$H =$ Enthalpy.

and hence

$$dG = dH - Tds - SdT$$

$$dH = dU + PdV + VdP$$

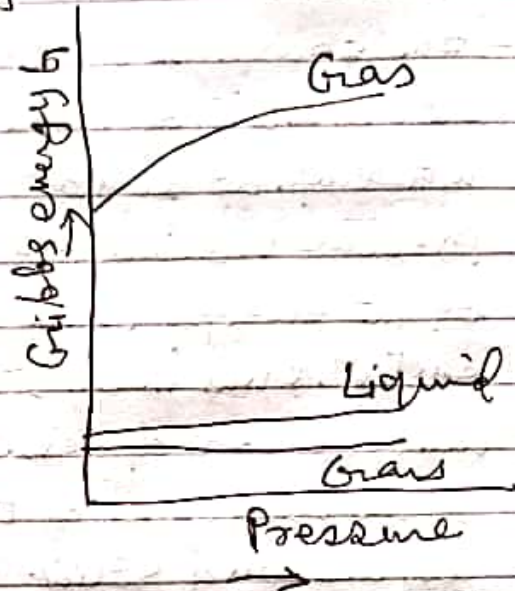
$$\text{i.e. } dG = dU + PdV + VdP - Tds - SdT$$

These ~~the~~ relationship shows G varies with temperature and pressure.

- 1) Temperature dependence of the Gibbs free energy (the Gibbs-Helmholtz equation) - The temp. dependence of G is governed by the following ~~the~~ relationship

$$\left(\frac{\partial G}{\partial T} \right)_P = -S$$

increases at constant temp. ~~Also~~ (G vs P graph)
The sensitivity of G to changes in P is greatest for gases and negligible for liquids and solids



We can find the change in the Gibbs energy due to a change in pressure at constant temperature through:

$$\Delta G = G(P_f) - G(P_i) = \int_{P_i}^{P_f} V dp$$

For solids and liquids we then treat V as constant, while for an ideal gas we use the $PV = nRT$ relationship and we get:-

$$G(P_f) = G(P_i) + \int_{P_i}^{P_f} \frac{nRT}{P} dp = G(P_i) + nRT \ln \left(\frac{P_f}{P_i} \right)$$

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