Helmholtz and Gibbs Energies

We had to consider the entropy change of both the system and its surroundings to determine the sign of $\Delta S_{universe}$ and establish whether a process is spontaneous or not. Although of great fundamental and theoretical importance, the criterion that $dS \geq 0$ for a spontaneous process is too restrictive for practical applications.

Let's consider a system with its volume and temperature held constant. The criterion that $dS \geq 0$ for a spontaneous process does not apply to a system at constant temperature and volume because the system is not isolated.; If the criterion $dS \geq 0$ does not apply, then what is the criterion for a spontaneous process that we can use for a system at constant temperature and volume?

Let's start with the expression of the First Law of thermodynamics,

$$dU = dQ + dW \longrightarrow (1)$$

$$dW = -PdV$$

$$\text{since } V = \text{const}; \; dW = 0$$

From clausius inequality,

$$dS \geq \frac{dQ}{T} \Rightarrow dQ \leq TdS$$

Thus, from (1),

$$dU \leq TdS \quad (\text{constant 'V'})$$

$$\Rightarrow \cancel{dU \leq +}\; dU - TdS \leq 0$$

$$\Rightarrow dU - d(TS) \leq 0 \quad (\text{constant 'T'})$$

$$\Rightarrow d(U - TS) \leq 0$$

$$\boxed{A = U - TS} \longrightarrow (2)$$

→ Helmholtz energy (Thermodynamic state function)

It is the analog of the criterion that $dS \geq 0$ for a spontaneous process to occur in an isolated system ⇐ ⇒

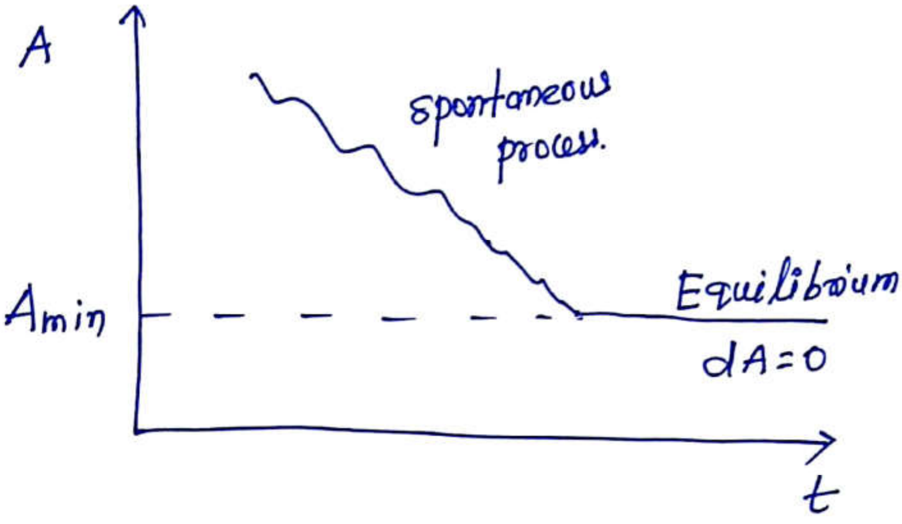
$$\boxed{dA \leq 0} \quad (\text{constant 'T' \& 'V'}) \longrightarrow (3)$$

In a system held at constant 'T' and 'V', the Helmholtz energy will decrease until all the possible spontaneous processes have occurred, at which time the system will be in equilibrium and 'A' will be a minimum. At equilibrium $dA = 0$.

For an isothermal change from one state to another,

$$\Delta A = \Delta U - T\Delta S \longrightarrow (4)$$

& $$\Delta A = \Delta U - T\Delta S \leq 0 \text{ (at constant 'T' \& 'V')} \longrightarrow (5)$$



For a reverssible path, $\Delta S = \frac{q_{rev}}{T}$

Thus, from (4),

$$\Delta A = \Delta U - q_{rev}$$

But from first law, $q_{rev} + W_{rev} = \Delta U$

$$\Delta U - q_{rev} = W_{rev}$$

Thus, $\boxed{\Delta A = W_{rev}}$ (isothermal, reversible) $\longrightarrow (6)$

If $\Delta A < 0$, the process will occur spontaneously and W_{rev} represents the work that can be done by the system if this change is carried out reversibly. This quantity is the maximum work that could be obtained.

If $\Delta A > 0$, the process will not occur spontaneously and W_{rev} represents the work that must be done on the system to produce the change in a reversible manner.

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Most reactions occur at constant pressure rather than at constant volume because they are open to the atmosphere. Let's see what the criterion of spontaneity is for a system at constant temperature and pressure.

From 1st law,

$$dQ + dW = dU$$

$$\Rightarrow dQ - PdV = dU$$

$$\Rightarrow dQ = dU + PdV$$

since, $\cancel{dQ}$ $dS \geq \frac{dQ}{T}$

$$\Rightarrow dQ \leq TdS$$

$$\Rightarrow dU + PdV \leq TdS$$

$$\Rightarrow dU + PdV - TdS \leq 0$$

$$\Rightarrow dU + d(PV) - d(TS) \leq 0$$

$$\Rightarrow d\left[\underbrace{U + PV - TS}\right] \leq 0$$

Gibbs Energy ⟵ $\boxed{G = U + PV - TS = H - TS}$ ⟶ (7)

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$\boxed{dG \lesseqgtr 0}$ (constant T & P)

$\longrightarrow (8)$

In a system at constant 'T' and 'P', the Gibbs energy will decrease as the result of any spontaneous processes until the system reaches equilibrium, where $dG = 0$.

Also,

$$\Delta G = \Delta H - T\Delta S \lesseqgtr 0 \quad \text{(constant 'T' \& 'P')}$$

The equality holds for a reversible process, whereas the inequality holds for an irreversible process.

The Third Law of thermodynamics

The entropy of a perfect crystalline substance is zero at ~~the~~ absolute zero temperature.

→ This allows us to determine the absolute entropy.

→ Entropy for substances are always positive.

$$\lim_{T \to 0} S = 0.$$

⇒ Principle of the unattainability of the absolute zero:

It is impossible by any procedure, no matter how idealized, to reduce any assembly to the absolute zero in a finite number of operations. and within a finite time.

⇒ ~~the~~ for any solid, let S_0 be the entropy at 0K and S be the entropy at TK, then

$$\Delta S = S - S_0 = \int_0^T \frac{C_p dT}{T}$$

Since, $S_0 = 0$ @ 0K, from 3rd law of thermo.

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

Lecture-31

For closed system,

$$(dG_i)_{T,P} \leqslant 0 \qquad \longrightarrow (1)$$

[consider a ~~sy~~ closed system composed of pure species 'i' in mechanical and thermal equilibrium and, therefore, at constant T and P.]

The subscripts "T" and "P" remind us that this expression is valid only at constant temperature and pressure, which are the criteria for thermal and mechanical equilibrium, respectively.

Eq^n. (1) says that for a spontaneous process, the Gibbs energy of a system at constant temp. and pressure always gets smaller (or stays the same); it never increases. The system wants to minimize its Gibbs energy. Equilibrium is the state at which the system no longer changes properties; therefore, equilibrium occurs at minimum Gibbs energy.

If we have two phases 'α' and 'β', we can write the total Gibbs energy of pure species 'i' as:

$$G_i = n_i^\alpha g_i^\alpha + n_i^\beta g_i^\beta \qquad \longrightarrow (2)$$

where n_i^α and n_i^β refer to the number of moles of 'i' in phases 'α' and 'β', respectively.

Differentiating Eq^n. (2) and applying Eq^n. (1), we get:

$$dG = n_i^\alpha \underset{\downarrow\, 0}{\cancel{dg_i^\alpha}} + g_i^\alpha dn_i^\alpha + n_i^\beta \underset{\downarrow\, 0}{\cancel{dg_i^\beta}} + g_i^\beta dn_i^\beta \leq 0 \quad \longrightarrow (3)$$

Two independent properties constrain the state of each phase of the pure substance i; thus, at a given T and P, g_i^α and g_i^β are constant. Consequently, the first and third terms of the above expression go to zero.

Since we have a closed system, a species leaving one phase must be added to the other phase, so.

$$n = n_i^\alpha + n_i^\beta$$

$$dn = dn_i^\alpha + dn_i^\beta$$

$$0 = dn_i^\alpha + dn_i^\beta$$

$$dn_i^\alpha = -dn_i^\beta \quad \longrightarrow (4)$$

using eq^n. (4) in eq^n. (3),

~~$g_i^\alpha dn_i^\alpha - g_i^\beta dn_i^\alpha \leq 0$~~

$$(g_i^\beta - g_i^\alpha) dn_i^\beta \leq 0 \quad \longrightarrow (5)$$

From eq^n. (5), we can infer how the species in a system respond to approach equilibrium.

Consider a system that initially has species in both phases 'α' and 'β'. If g_i^β is larger than g_i^α, dn_i^β must be less than zero to satisfy the inequality. Physically, species 'i' will transfer from phase 'β' to phase 'α', lowering the Gibbs energy of the system. Conversely if g_i^α is greater than g_i^β, species 'i' will transfer from phase 'α' to phase 'β'. However, if the Gibbs energies of both phases are equal, Eq^n. (5) becomes an equality and the system has no impetus to change. This condition represents equilibrium. Thus, the criterion for chemical equilibrium is when the Gibbs energy is at the minimum:

$$g_i^\alpha = g_i^\beta \longrightarrow (6)$$

In differential form,

$$dg_i^\alpha = dg_i^\beta \longrightarrow (7)$$

[consider a system with two phases in equilibrium at a given 'T' and 'P'. For a small change in the equilibrium temp. dT and in equilibrium pressure dP, the differential changes in Gibbs energy of each phase must be equal:]

Applying the fundamental property relation for 'g' to each phase, we get:

$$v_i^\alpha dp - s_i^\alpha dT = v_i^\beta dp - s_i^\beta dT \longrightarrow (8)$$

Rearrangement yields:

$$\Rightarrow v_i^\alpha dp - v_i^\beta dp = s_i^\alpha dT - s_i^\beta dT$$

$$\Rightarrow (v_i^\alpha - v_i^\beta) dp = (s_i^\alpha - s_i^\beta) dT$$

$$\Rightarrow \frac{dP}{dT} = \frac{s_i^\alpha - s_i^\beta}{v_i^\alpha - v_i^\beta} \longrightarrow (9)$$

Now we can also apply eqn. (6):

$$g_i^\alpha = g_i^\beta$$

By the definition of Gibbs energy,

$$h_i^\alpha - Ts_i^\alpha = h_i^\beta - Ts_i^\beta$$

$$\Rightarrow h_i^\alpha - h_i^\beta = Ts_i^\alpha - Ts_i^\beta$$

$$\Rightarrow s_i^\alpha - s_i^\beta = \frac{h_i^\alpha - h_i^\beta}{T} \longrightarrow (10)$$

Substitution of eqn. (10) in eqn. (9) yields the <u>clapeyron equation</u>:

$$\frac{dP}{dT} = \frac{h_i^\alpha - h_i^\beta}{(v_i^\alpha - v_i^\beta)T} \longrightarrow (11)$$

Pure Component vapor-liquid Equilibrium: The clausius-clapeyron Equation

Next we consider the specific case of vapor-liquid Equilibrium.

In this case, the molar volume of the liquid is often negligible compared to the volume of the vapor:

$$v_i^l << v_i^v \quad \text{or} \quad v^l \approx 0 \qquad \text{(Assumption I)}$$

If additionally we consider the vapor to obey the ideal gas model,

$$v_i^v = \frac{RT}{P} \qquad \text{(Assumption II)}$$

Thus, Eq^n. (11) becomes-

$$\frac{dP_i^{sat}}{dT} = \frac{\Delta h_{vap,i} \, P_i^{sat}}{RT^2} \longrightarrow (12)$$

where $\Delta h_{vap,i} = h_i^v - h_i^l$ and P_i^{sat} represent the enthalpy of vaporization and the saturation pressure, respectively, of species 'i' at temp. T.

Separating variables,

$$\frac{dP_i^{sat}}{P_i^{sat}} = \frac{\Delta h_{vap,i}\, dT}{RT^2} \longrightarrow (13)$$

Eq^n. (13) is called the clausius-clapeyron equation.

It can be rewritten in the form

$$d \ln P_i^{sat} = -\frac{\Delta h_{vap,i}}{R} d\left(\frac{1}{T}\right) \longrightarrow (14)$$

If we assume the enthalpy of vaporization is independent of temperature, that is

$$\Delta h_{vap,i} \neq \Delta h_{vap,i}(T) \qquad \text{(Assumption III)}$$

we can either definitely integrate Eq^n. (14) between state 1 and state 2 to get:

$$\ln \frac{P_2^{sat}}{P_1^{sat}} = -\frac{\Delta h_{vap,i}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \longrightarrow (15)$$

or write the indefinite integral of Eq^n. (14):

$$\ln P_i^{sat} = \text{const.} - \frac{\Delta h_{vap,i}}{RT} \longrightarrow (16)$$

In fact, Assumption III is not valid over large temperature ranges. The enthalpy of vaporization decreases as temperature increases. So, eq^n. (15) & (16) can be used only over a limited temp. range. However, in surprisingly many cases, the error introduced by Assumption III is approximately offset by the errors of Assumption I and II, leading to linear behavior of $\ln P^{sat}$ vs. $1/T$ over a larger range.

(Lecture-47)

Q.1 For two species, A and B, with a positive enthalpy change of mixing:

(a) Are the like interactions or the unlike interactions stronger?

Solution: like interaction is more stable and more strong than unlike interaction.

Q.2 One mole of pure species exists in liquid-vapor equilibrium in a rigid container of volume $V = 1L$, a temp. of 300 K, and a pressure of 1 bar. The enthalpy of vaporization and the second virial co-efficient are:

$$\Delta h_{vap} = 16628 \ J/mol \ ; \ B' = -1\times10^{-7} \ m^3/J$$

Assume the enthalpy of vaporization does not change with temp. You may neglect the molar volume of the liquid relative to that of the gas.

(a) ~~How many moles of vapor are there?~~ This container is heated until the pressure reaches 2 bar and is allowed to reach equilibrium. Both vapor and liquid phases are still present. Find the final temp. of this system.

Solution: we have,

$$\frac{dP}{dT} = \frac{\Delta h^{vap}}{(v^{v}-v^{l})T} \longrightarrow (1)$$

Since, molar volume of liquid is negligible compared to that of the gas,

$$v^{v}-v^{l} \simeq v^{v}$$

Thus,

$$\frac{dP}{dT} = \frac{\Delta h^{vap}}{v^{v}T} \longrightarrow (2)$$

Also,

$$z = \frac{Pv^{v}}{RT} = 1 + B'P$$

$$\Rightarrow v^{v} = \frac{RT}{P}(1+B'P) = RT\left(\frac{1}{P}+B'\right)$$

substituting v^{v} in eqn. (2),

$$\frac{dP}{dT} = \frac{\Delta h^{vap}}{RT\left(\frac{1}{P}+B'\right)T} = \frac{\Delta h^{vap}}{RT^{2}\left(\frac{1}{P}+B'\right)}$$

$$\Rightarrow \left(\frac{1}{P}+B'\right)dP = \frac{\Delta h^{vap}}{RT^{2}}dT$$

integrating,

$$\int_{1\,bar}^{21\,bar}\left(\frac{1}{P}+B'\right)dP = \frac{\Delta h^{vap}}{R}\int_{300K}^{T_2}\frac{dT}{T^{2}}$$

$$\Rightarrow \int_{1}^{21}\frac{dP}{P} + B'\int_{1}^{21}dP = \frac{\Delta h^{vap}}{R}\left(-\frac{1}{T}\right)_{300}^{T_2}$$

$$\Rightarrow \ln\left(\frac{21}{1}\right) + B'(21-1)\,\text{bar} = \frac{\Delta h^{vap}}{R}\left[-\frac{1}{T_2}+\frac{1}{300}\right]$$

$$\Rightarrow 3.045 + \left(-10^{-7}\frac{m^3}{J}\right)\left(20\times10^{5}\frac{N}{m^2}\right) = \frac{16628\ J/mol}{8.314\ J/mol\,K}\left[\frac{1}{300}-\frac{1}{T_2}\right]$$

$$\Rightarrow \boxed{T_2 = 523.3\,K}$$ Solution.

[Q.3] The vapor pressure of silver (between 1234 K and 2485 K) is given by the following expression:

$$\ln P^{sat} = -\frac{14260}{T} - 0.458\ln T + 12.23$$

where 'P' in torr and 'T' in K. Estimate the enthalpy of vaporization at 1500K.

Solution: we have,

$$\frac{dP^{sat}}{dT} = \frac{\Delta h^{vap}P^{sat}}{RT^2} \longrightarrow (1)$$

given-

$$\ln P^{sat} = \frac{-14260}{T} - 0.458\ln T + 12.23$$

$$P^{sat} = \exp\left[\frac{-14260}{T} - 0.458\ln T + 12.23\right] \rightarrow (2)$$

Differentiate eqn. (2) w.r.t. temp,

$$\frac{dp^{sat}}{dT} = \exp\left(-\frac{14260}{T} - 0.458\ln T + 12.23\right)\left(\frac{14260}{T^2} - \frac{0.458}{T}\right)$$

$$\Rightarrow \frac{dp^{sat}}{dT} = p^{sat}\left[\frac{14260}{T^2} - \frac{0.458}{T}\right] \longrightarrow (3)$$

using eqn. (3) in eqn. (1), we get-

$$p^{sat}\left[\frac{14260}{T^2} - \frac{0.458}{T}\right] = \frac{p^{sat}\Delta h^{vap}}{RT^2}$$

$$\Rightarrow \Delta h^{vap} = RT^2\left[\frac{14260}{T^2} - \frac{0.458}{T}\right]$$

$$= 14260R - 0.458RT$$

$$= 14260(8.314\ J/mol\,K) - 0.458(8.314\ J/mol\,K)(1500\ K)$$

$$= 112845\ J/mol$$

$$\boxed{\Delta h^{vap} = 112.845\ KJ/mol}$$ Ans.

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[Q.4] At a temp. of 60.6°c, benzene exerts a saturation pressure of 400 torr. At 80.1°c, its saturation pressure is 760 torr. using these data, estimate the enthalpy of vaporization of benzene. Compare it to the reported value of $\Delta h_{vap} = 35$ KJ/mol.

Sol^n we have,

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = \frac{-\Delta h^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Given, $T_1 = 60.6 + 273 = 333.6$, $P_1^{sat} = 400$ torr.

$T_2 = 353.1\,K$, $P_2^{sat} = 760$ torr.

$R = 8.314$ J/mol-K

using these values,

$$\ln\left(\frac{760}{400}\right) = \frac{-\Delta h^{vap}}{(8.314\ J/mol\,K)}\left[\frac{1}{353.1} - \frac{1}{333.6}\right]$$

$$\Delta h^{vap} = \cancel{33}\,32235\ J/mol$$

$$\boxed{\Delta h^{vap} = 32.24\ KJ/mol.}$$ Ans.

[~~Q.5~~] % deviation from exp. data $= \left(\frac{35 - 32.24}{35}\right) \times 100$

$= \underline{7.9\%}$ Ans

i.e. Experimental value is 7.9% higher than that of calculated value.

[Q.5] Pure ethanol boils at a temperature of 63.5°c at a Pressure of 400 torr. It also boils at 78.4°c and 760 to Using these data, estimate the saturation pressure for ethanol at 100°c.

Solution: we have,

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = -\frac{\Delta h^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Given, $T_1 = 273+63.5 = 336.5\,K$, $P_1^{sat} = 400$ torr.

$T_2 = 273+78.4 = 351.4\,K$, $P_2^{sat} = 760$ torr.

using these data,

$$\ln\left(\frac{760}{400}\right) = -\frac{\Delta h^{vap}}{(8.314\ J/mol\,K)}\left[\frac{1}{351.4} - \frac{1}{336.5}\right]$$

$$\therefore \Delta h^{vap} = 42349\ J/mol$$

$$= \underline{\underline{42.35\ kJ/mol.}}$$

Now, we have to find, P_3^{sat} at $T_3 = 373\,K$.

$$\ln\left(\frac{P_3^{sat}}{P_1^{sat}}\right) = -\frac{42349}{8.314}\left[\frac{1}{T_3} - \frac{1}{T_1}\right]$$

$$\underline{\underline{P_3^{sat} = 1759\ torr.}}$$