G ; FREE ENERGY — "Energy free to do Work"

Free Energy – thermodynamic term that may be used to judge spontaniety

— At constant p + T (useful term b/c most reactions occur at constant p + T ! (more useful than S) shows dependence of S on Temp.

G = H – TS

in K

ΔG = ΔH - TΔS — At constant temp. — All from system perspective

How relate to spontaneity?

$$\frac{\Delta G}{-T} = \frac{\Delta H}{-T} - \frac{T\Delta S}{-T} \quad \text{divide all by } -T$$

— At constant T + P

$$\frac{\Delta G}{-T} = -\frac{\Delta H}{T} + \Delta S \qquad \Delta S_{surr} = \frac{-\Delta H}{T}$$

+ ΔG Not Spontaneous $= \Delta S_{surr} + \Delta S = \Delta S_{univ}$ ∴ $\boxed{\Delta S_{univ} = \frac{-\Delta G}{T}}$ at constant T & P

- ΔG Spontaneous

shows that process is spontaneous only when ΔG is neg.

−ΔG means $+\Delta S_{univ}$.

Ex: $H_2O_{(s)} \rightarrow H_2O_{(l)}$

$\Delta H^\circ = 6.03 \times 10^3 \frac{J}{mol}$

$\Delta S^\circ = 22.1 \frac{J}{K \cdot mol}$

$-\Delta G = \Delta H - T\Delta S$

−10°C = +2.2×10² = G

0°C = 0 = G (eq.)

+10°C = −2.2×10²

opposite direction favored

−10°C = 263K

$\Delta G = \Delta H - T\Delta S$

$= (6.03 \times 10^3 \frac{J}{mol}) - (263K)(22.1 \frac{J}{K \cdot mol})$

$= 218. \frac{J}{mol}$ Non spontaneous

0°C = 273K

$\Delta G = \Delta H - T\Delta S$

$= (6.03 \times 10^3 \frac{J}{mol}) - (273)(22.1 \frac{J}{K \cdot mol})$

$= -3.3 \approx 0$

Equilib (when ΔG = 0)

+10°C = 283K

$\Delta G = \Delta H - T\Delta S$

$= (6.03 \times 10^3 \frac{J}{mol}) -$ (283)(22.1 J/K·mol)

$= -224. \frac{J}{mol}$

Spontan.

Table 16.4

at any temp, process is not favored energetically ~
does occur at 18°C b/c $-\Delta G$

Table 16.5

Ex 16.5: At what temperature is the following process spontaneous at 1.0 atm?

$Br_{2(l)} \rightarrow Br_{2(g)}$

$\Delta H^o = 31.0$ kJ/mol and $\Delta S^o = 93.0$ J/K.mol

What is the normal boiling point of liquid Br_2?

Vap spontaneous at all temps where $-\Delta G$

ΔH° ~ not favorable

ΔS° ~ favorable

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At b.pt. ~ these will balance ~ eg $\therefore \Delta G = 0$

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$T\Delta S = \Delta H$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{3.10 \times 10^4 \frac{J}{mol}}{93.0 \frac{J}{K \cdot mol}} = 333K$$

Temp Spontaneous ~

↑ 333K

then $T\Delta S$ greater than ΔH

↓ 333K ~ not spontaneous

ΔH controls