

# G ; FREE ENERGY

"Energy Free to do Work"

At constant P & T more useful processes occur at constant P & T! (more useful than S) shows dependence of S on Temp.

Free Energy - thermodynamic term that may be used to judge spontaneity

$$G = H - TS$$

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

At constant temp. All from system perspective

How relate to spontaneity?

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

$$\frac{\Delta G}{-T} = -\frac{\Delta H}{T} + \Delta S \quad \Delta S_{\text{surv}} = \frac{-\Delta H}{T}$$

At constant T & P

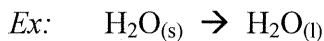
+ ΔG Not spontaneous = ΔS<sub>surv</sub> + ΔS = ΔS<sub>univ</sub> ∴

- ΔG Spontaneous

- ΔG means + ΔS<sub>univ</sub>.

$$\Delta S_{\text{univ}} = \frac{-\Delta G}{T} \quad \text{at constant } T \neq P$$

shows that process is spontaneous only when ΔG is neg.



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

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

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

$$-10^\circ\text{C} = +2.2 \times 10^2 = G$$

$$0^\circ\text{C} = 0 = G \text{ (eq.)}$$

$$+10^\circ\text{C} = -2.2 \times 10^2$$

opposite direction favored

-10°C = 263K

0°C = 273K

+10°C = 283K

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

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

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

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

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

$$= -3.3 \approx 0$$

Equilib (when ΔG=0)

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

$$= (6.03 \times 10^3 \frac{\text{J}}{\text{mol}}) -$$

$$(283)(22.1 \frac{\text{J}}{\text{K}\cdot\text{mol}})$$

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

Spontaneous

process is up, means doing the work

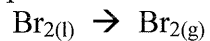
Table 16.4

at any temp, process is not  
favored energetically ~  
does occur at 10°C /c

Table 16.5

-ΔG

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



$$\Delta H^\circ = 31.0 \text{ kJ/mol} \quad \text{and} \quad \Delta S^\circ = 93.0 \text{ J/K}\cdot\text{mol}$$

What is the normal boiling point of liquid  $\text{Br}_2$ ?

Uap spontaneous at all temp where  $-\Delta G$

$\Delta H^\circ \sim$  not favorable

$\Delta S^\circ \sim$  favorable

At b.p.  $\sim$  these will balance  $\sim$  eg  $\therefore \Delta G = 0$

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

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

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

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

Temp Spontaneous  $\sim$

$\uparrow$  333K

then  $T\Delta S$  greater than  $\Delta H$

$\downarrow$  333K  $\sim$  not spontaneous  
 $\Delta H$  controls

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