4/15/2019

Spontaneous if ... $\Delta S_{UNIV} \geq 0$

or ... $\Delta G \leq 0$

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

ΔH	ΔS	ΔG	
		$\Delta H - T\Delta S$	
-ve	+ve	$\underbrace{(-) - (+)}_{(-)}$	always spont!
		$\Delta H - T\Delta S$	
+ve	-ve	$\underbrace{(+) - (-)}_{(+)}$	always non-spont!
		$\Delta H - T\Delta S$	
-ve	-ve	$(-) \underbrace{- (-)}$	@ low T, $\Delta G < 0$ (-ve), spont
		$(-) + (+)$	@ high T, $\Delta G > 0$ (+ve), non-spont
		$\Delta H - T\Delta S$	
+ve	+ve	$\underbrace{(+)}\ \underbrace{-(+)}$	@ low T, $\Delta G > 0$ (+ve), non-spont
		$\oplus + \ominus$	@ high T, $\Delta G < 0$ (-ve), spont.

ex: $CCl_4(g) \longrightarrow C(s,\text{graphite}) + 2Cl_2(g)$

$\Delta H = +95.7\ kJ$

$\Delta S = +142.2\ J/K$

made more gas molec. $\Delta S > 0$

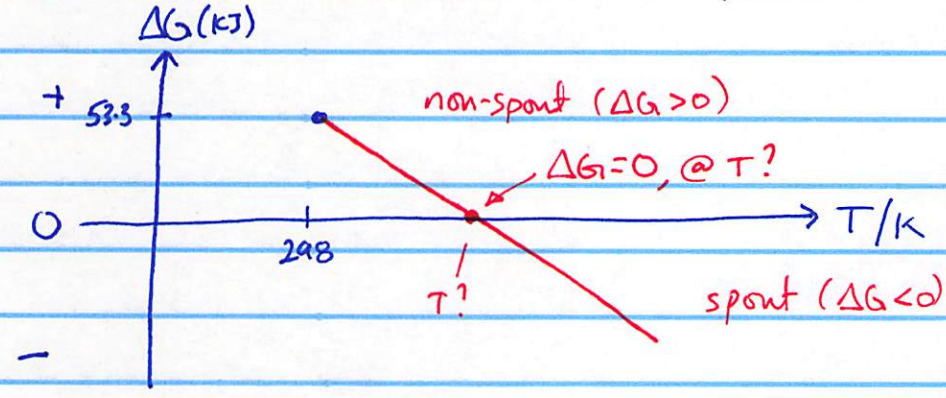
(a) What's ΔG @ 25°C? (298.15K) Spont/Non-spont?

$$\Delta G = \Delta H - T\Delta S = +95.7\,kJ - 298.15\,\cancel{K} \cdot +142.2\,\frac{\cancel{J}}{\cancel{K}} \times \frac{kJ}{10^3\,\cancel{J}}$$

$$= +53.3\,kJ$$

NON-SPONT!

Q: What T is needed to become spont?



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

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{+95.7\,kJ \times \frac{10^3\,J}{kJ}}{142.2\,J/K}$$

$$\frac{1}{1/K} = 1 \times \frac{K}{1}$$

$= 673\ K$ (3 s.f.)

(400.°C)

Very powerful tool... $\Delta G \leq 0$, spont!

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

? ?

how do we calculate?

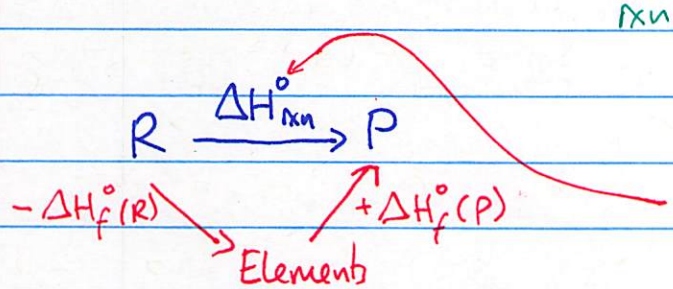
Ch6: $$\Delta H^\circ_{rxn} = \left[\sum_i n_p \cdot \Delta H^\circ_f (\text{Prods})\right] - \left[\sum_i n_r \cdot \Delta H^\circ_f (\text{Reacts})\right]$$

#mol prods (coeff.)

#mol reacts.

standard enthalpy of formation

rxn: Elements $\longrightarrow$ substance ; ΔH° (1 mol)



STD state symbol

s/l ~ pure

g ~ 1 atm

aq ~ 1 M

Can calculate ΔS°_{rxn} using similar idea!

3rd law of thermodynamics

@ T=0, S=0

Can calculate $\Delta S^\circ_{rxn} = [\sum n_p \cdot S^\circ(\text{products})] \ominus [\sum n_r \cdot S^\circ(\text{reacts.})]$ (std conditions)

let's find: ΔH°_{rxn}, ΔS°_{rxn}, and ΔG°_{rxn} for:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

@25°C, @125°C

Substance	$NH_3(g)$	$O_2(g)$	$NO(g)$	$H_2O(g)$
ΔH_f° (kJ/mol)	-45.9	∅	91.3	-241.8
S° (J/mol·K)	192.8	205.2	210.8	188.8

$$\Delta H^\circ_{rxn} = \left[4\,\text{mol} \times 91.3\tfrac{kJ}{mol} + 6\,\text{mol} \times -241.8\tfrac{kJ}{mol}\right] - \left[4\,\text{mol} \times -45.9\tfrac{kJ}{mol} + 5\,\text{mol} \times \emptyset\right]$$

$$= -902.0\,kJ$$

$$\Delta S^\circ_{rxn} = \left[4\,\text{mol} \times 210.8\tfrac{J}{mol\cdot K} + 6\,\text{mol} \times 188.8\tfrac{J}{mol\cdot K}\right] - \left[4\,\text{mol} \times 192.8\tfrac{J}{mol\cdot K} + 5\,\text{mol} \times 205.2\tfrac{J}{mol\cdot K}\right]$$

$$= +178.8\,J/K$$

$$\Delta G^\circ_{rxn} = -902.0\,kJ - 298.15\,K \times +\frac{178.8\,J}{K} \times \frac{kJ}{10^3\,J} = -955.5\,kJ$$

$\Delta H - T\Delta S$

So, it is spontaneous!

@125°C, $\Delta G^\circ = -973.2\,kJ$

Perfect crystal at 0 K

$W = 1 \qquad S = 0$

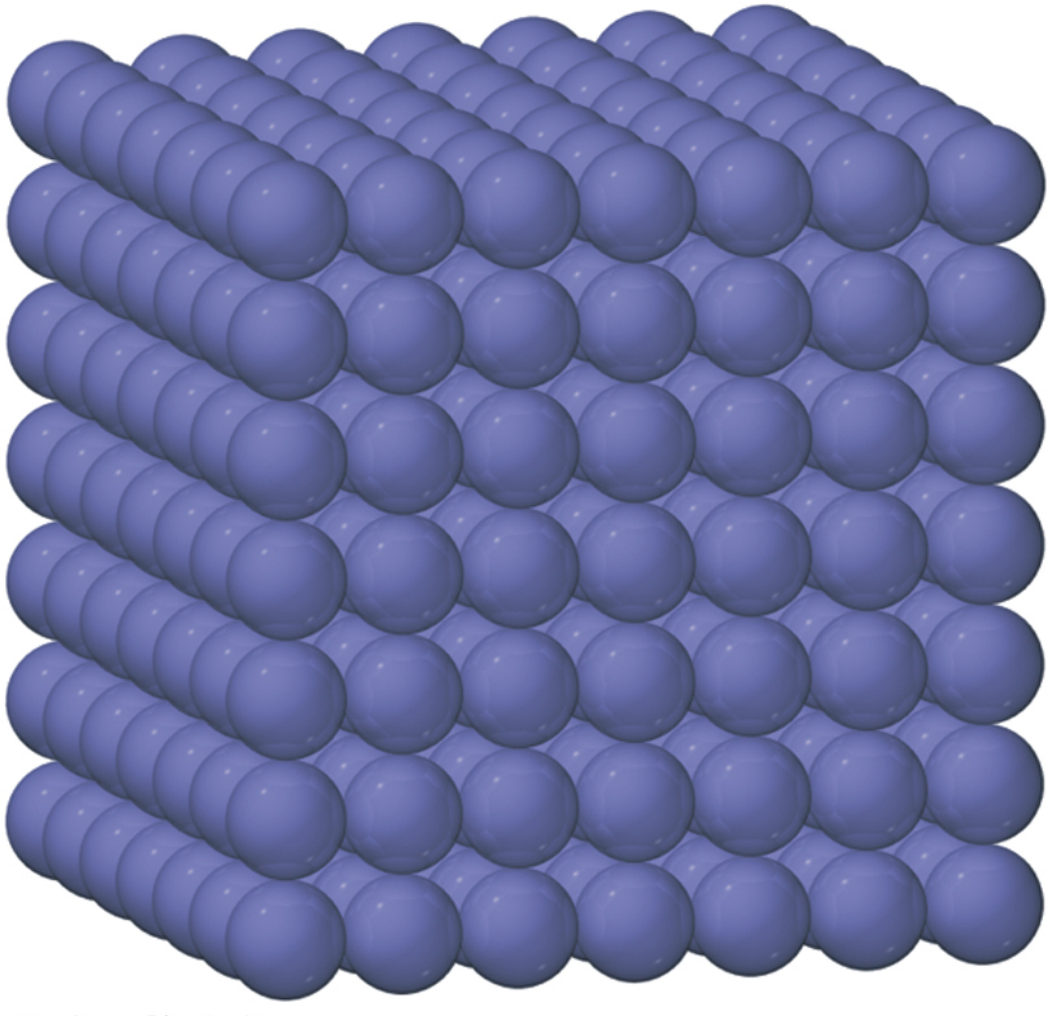


TABLE 18.2 Standard Molar Entropy Values ($S°$) for Selected Substances at 298 K

Substance	$S°$ (J/mol · K)	Substance	$S°$ (J/mol · K)	Substance	$S°$ (J/mol · K)
Gases		**Liquids**		**Solids**	
$H_2(g)$	130.7	$H_2O(l)$	70.0	MgO(s)	27.0
Ar(g)	154.8	$CH_3OH(l)$	126.8	Fe(s)	27.3
$CH_4(g)$	186.3	$Br_2(l)$	152.2	Li(s)	29.1
$H_2O(g)$	188.8	$C_6H_6(l)$	173.4	Cu(s)	33.2
$N_2(g)$	191.6			Na(s)	51.3
$NH_3(g)$	192.8			K(s)	64.7
$F_2(g)$	202.8			NaCl(s)	72.1
$O_2(g)$	205.2			$CaCO_3(s)$	91.7
$Cl_2(g)$	223.1			$FeCl_3(s)$	142.3
$C_2H_4(g)$	219.3				