PHYSICAL CHEMISTRY I

NANIK DWI NURHAYATI,S.SI, M.SI

nanikdn.staff.uns.ac.id

nanikdn.staff.fkip.uns.ac.id

081556431053 / (0271) 821585

Chemical Thermodynamics

KESPONTANAN, DAN KESETIMBANGAN

Hukum termodinamika kedua, entropi semesta (sistem + lingkungan) selalu naik pada proses spontan dan tidak berubah pada proses kesetimbangan.

$S_{semesta} = S_{sis} + S_{ling} > 0$ proses spontan

$S_{semesta} = S_{sis} + S_{ling} = 0$ proses kesetimbangan

$S_{universe} = S_{sistem} + S_{lingkungan}$

Kesetimbangan $\Delta S_{universe} = \Delta S_{sistem} + \Delta S_{lingkungan} = 0$

$S_{sistem} = - S_{lingkungan}$

Tanda dari ΔH dan Kespontanan

Semua reaksi pembakaran adalah spontan dan eksotermik:

$$CH_{4\,(g)} + 2\,O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2\,H_2O_{(g)} \qquad \Delta H^o_{rxn} = -802\ kJ$$

Besi berkarat secara spontan and eksotermik:

$$2\,Fe_{(s)} + \frac{3}{2}\,O_{2\,(g)} \longrightarrow Fe_2O_{3\,(s)} \qquad \Delta H^o_{rxn} = -826\ kJ$$

Senyawa ion secraa spontan membentuk unsurnya dgn melepas kalor:

$$Na_{(s)} + \frac{1}{2}\,Cl_{2\,(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H^o_{rxn} = -411\ kJ$$

Pd tekanan normal, air membeku di bawah 0° C dan mencair di atas 0° C. keduanya adalah proses spontan, namun yang pertama termasuk eksotermik sedangkan yang kedua termasuk endotermik.

$$H_2O_{(l)} \longrightarrow H_2O_{(s)} \qquad \Delta H^o_{rxn} = -6{,}02\ kJ$$

(eksotermik; spontan pada $T < 0^oC$)

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \qquad \Delta H^o_{rxn} = +6{,}02\ kJ$$

(endotermik; spontan pada $T > 0^oC$)

Free Energy and Equilibrium

- Equilibrium occurs at the lowest value of free energy available to the reaction system, when $\Delta G = 0$

- At equilibrium, $\Delta G = 0$, $Q = K_{eq}$ so

  $\Delta G = 0 = \Delta G^o + RT \ln K_{eq}$

  $\Delta G^o = - RT \ln K_{eq}$

- Use this equation to find K_{eq} given ΔG^o, or to find ΔG^o given K_{eq}

- Relationship between ΔG^o and K_{eq}

ΔG^o	K_{eq}
= 0	1
< 0	>1
> 0	< 1

GIBBS FREE ENERGY

At constant T and P

$$\Delta G \equiv \Delta H - T\Delta S \Rightarrow -\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

$$\text{Q} \quad \Delta S_{surr} = -\frac{\Delta H}{T} \quad \therefore \quad -\frac{\Delta G}{T} = \Delta S_{surr} + \Delta S_{sys} = \Delta S_{univ}$$

$\Delta G < 0$ spontaneous

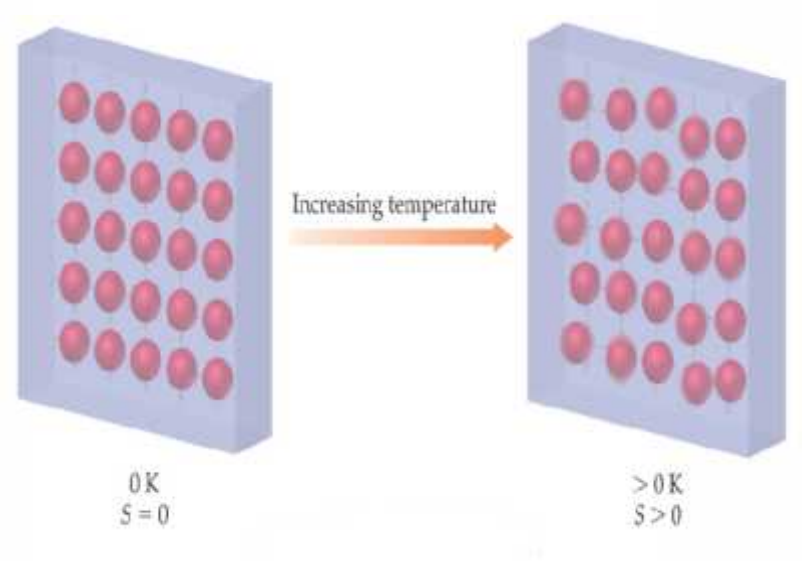
$\Delta G = 0$ equilibrium

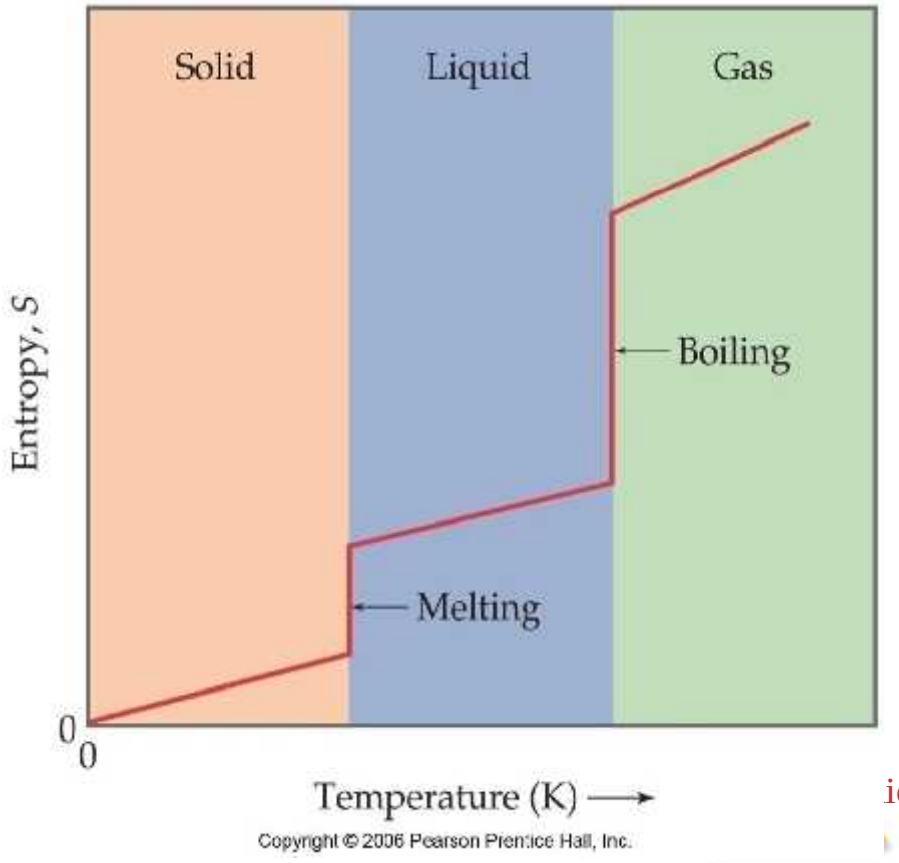
$\Delta G > 0$ non-spontaneous

THIRD LAW OF THERMODYNAMICS

The entropy of a pure crystalline substance at absolute zero is 0.

$$S = k\ ln W = k\ ln 1 = 0$$





ics

Standard Molar Entropies / ΔS^o_{rxn}

$aA + bB \rightarrow cC + dD$ (25°C)

$$\Delta S^o_{reaction} = \sum S^o_{prod.} - \sum S^o_{react.}$$

$$= (c\Delta S^0_C + d\,\Delta S^0_D) - (a\Delta S^0_A + b\,\Delta S^0_B)$$

$$\Delta S^o_{rxn} = \Sigma m\, S^o_{product} - \Sigma n\, S^o_{reactant}$$

$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$

ΔS^o_{rxn} = (2 mol NH_3 x S^o NH_3) – [(1 mol N_2 x S^o N_2) + (3 mol H_2 x S^o H_2)]

ΔS^o_{rx} = (2 x 193) – [(1 x 191,5) + (3 x 130,6) = -197 J/K

Standard Molar Entropies

Substance	S° (J/K·mol)	Substance	S° (J/K·mol)
C (diamond)	2.37	HBr (g)	198.59
C (graphite)	5.69	HCl (g)	186.80
CaO (s)	39.75	HF (g)	193.67
$CaCO_3$ (s)	92.9	HI (g)	206.33
C_2H_2 (g)	200.82	H_2O (l)	69.91
C_2H_4 (g)	219.4	H_2O (g)	188.72
C_2H_6 (g)	229.5	NaCl (s)	72.12
CH_3OH (l)	127	O_2 (g)	205.03
CH_3OH (g)	238	SO_2 (g)	248.12
CO (g)	197.91	SO_3 (g)	256.72

STANDARD FREE ENERGY CHANGES

Standard free energies of formation, ΔG_f° are analogous to standard enthalpies of formation, ΔH_f°. $\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$

$$\Delta G^o_{rxn} = \Sigma m \Delta G^o_{f(produk)} - \Sigma n \Delta G^o_{f(reaktan)}$$

$$\Delta S^0_{reaction} = \sum S^0_{products} - \sum S^0_{reactants}$$

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

ΔG° can be looked up in tables,*or* calculated from S° and aHî.

THE TEMPERATURE DEPENDENCE OF K

$$\Delta G^0 = -RT\ln(K) = \Delta H^0 - T\Delta S^0$$

$$\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} = -\frac{\Delta H^0}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^0}{R}$$

$$\ln(K_2) = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$$

$$\ln(K_1) = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$