PHYSICAL CHEMISTRY I

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Chemical
Thermodynamics

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

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

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

$\Delta G < 0$ spontaneous

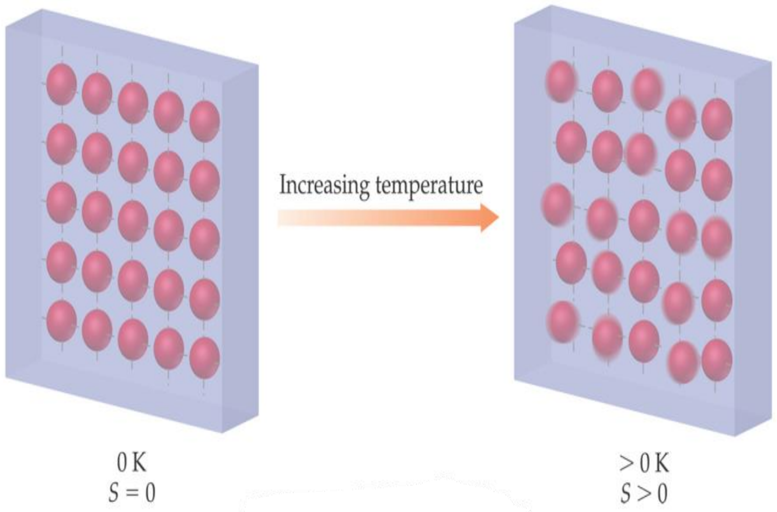
$\Delta G = 0$ equilibrium

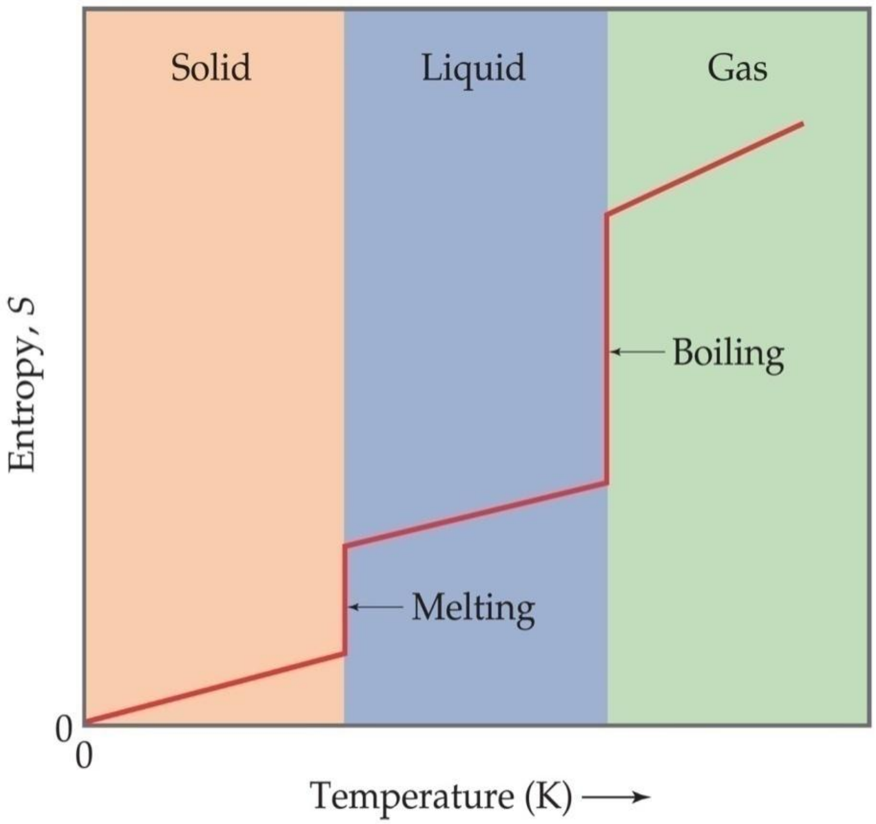
$\Delta G > 0$ non-spontaneous

THIRD LAW OF THERMODYNAMICS

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

$$S = k\, lnW = k\, ln1 = 0$$





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Standard Molar Entropies / ΔS^o_{rxn}

$aA + bB \rightarrow cC + dD$ (25°C)

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

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

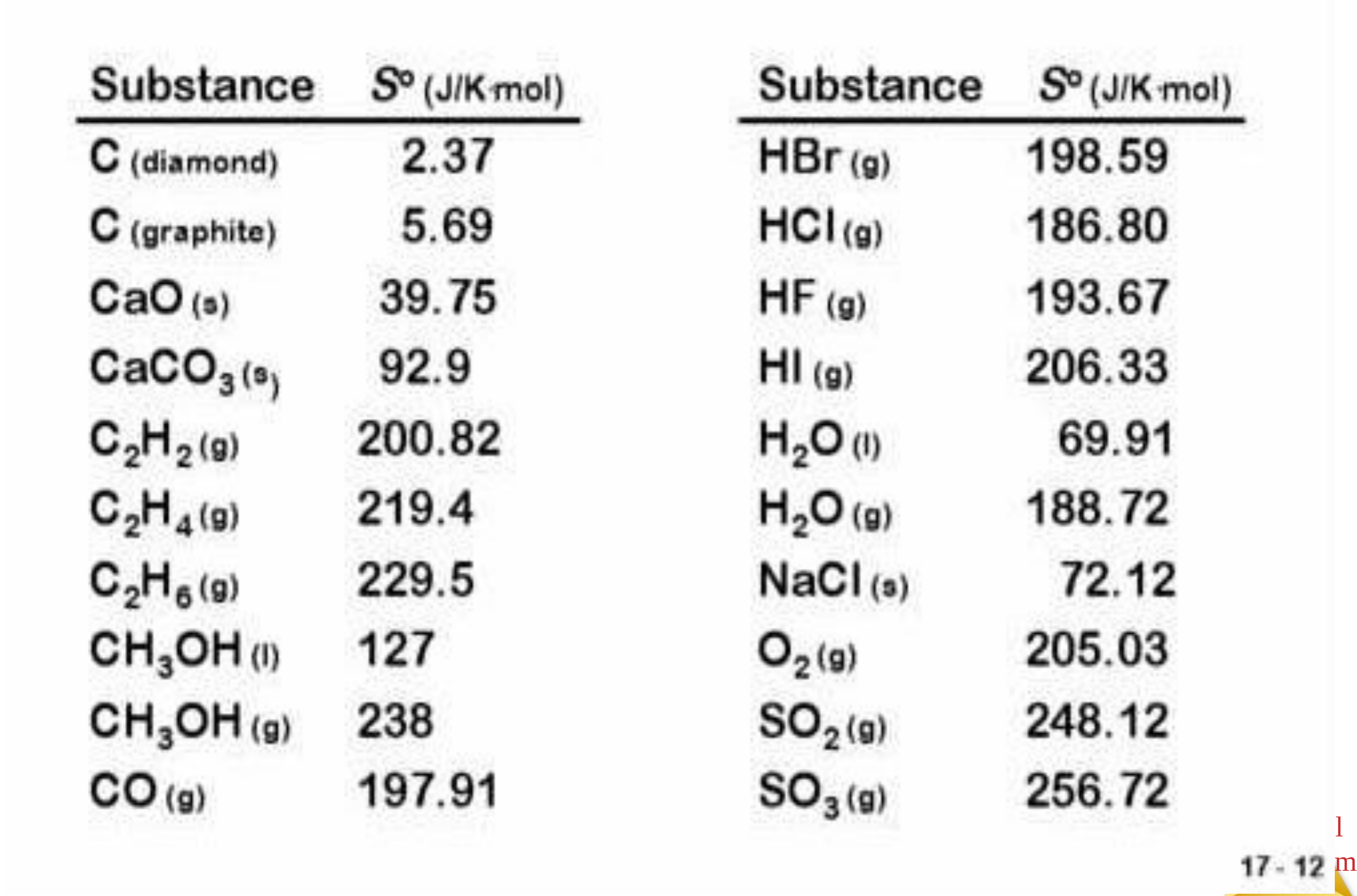
$$\Delta S^o_{rxn} = \Sigma m\ S^o_{product} - \Sigma n\ S^o_{reactant}$$

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

$\Delta S^o_{rxn} = (2\ mol\ NH_3 \times S^o\ NH_3) - [(1\ mol\ N_2 \times S^o\ N_2) + (3\ mol\ H_2 \times S^o\ H_2)]$

$\Delta S^o_{rx} = (2 \times 193) - [(1 \times 191{,}5) + (3 \times 130{,}6) = -197\ J/K$

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 ΔH°.

THE TEMPERATURE DEPENDENCE OF K

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

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

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

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

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