Formulas and Constants in Chemical Thermodynamics

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First Law

$$dE = dQ + dW \tag{1}$$

Second Law

$$dS \geq \frac{dq}{T} \tag{2}$$

Third Law

$$\lim_{T \to 0} (\Delta G - \Delta H) = 0 \tag{3}$$

$$\lim_{T \to 0} -T\Delta S = 0 \tag{4}$$

System of Constant Composition

$$U = Q + W \tag{5}$$
$$H = U + PV \tag{6}$$
$$A = U - TS \tag{7}$$
$$G = H - TS \tag{8}$$

Gibbs Equations

$$dU = TdS - PdV \tag{9}$$
$$dH = TdS + VdP \tag{10}$$
$$dA = -SdT - PdV \tag{11}$$
$$dG = -SdT + VdP \tag{12}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \quad C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{13}$$

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_P \tag{14}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad V = \left(\frac{\partial H}{\partial P}\right)_S \tag{15}$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_V \quad -P = \left(\frac{\partial A}{\partial V}\right)_T \tag{16}$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_P \quad V = \left(\frac{\partial G}{\partial P}\right)_T \tag{17}$$

Euler's Reciprocity Relation

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{18}$$

Using **Euler's Reciprocity Relation** one arrives at **Maxwell Relations**.

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{19}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{20}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{21}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{22}$$

$$\Delta H^\circ = \Delta U^\circ + RT \sum_i \nu_i(g) \tag{23}$$

Clausius-Clapeyron

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{24}$$

Van der Waals

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{25}$$

Ideal Solutions

$$\mu_i = \mu_i^\circ + RT ln \chi_i \tag{26}$$

Kinetic Theory of Gases

Ideal Monoatomic Gas

$$C_v = \frac{3}{2}R \tag{27}$$

$$C_p = \frac{5}{2}R \tag{28}$$

Rate Laws

First Order

$$\frac{d[A]}{dT} = -k_A[A]$$

$$\int \frac{d[A]}{[A]} = -k_A$$

$$ln\frac{[A]}{[A]_0} = -k_A(t2 - t1)$$

$$[A] = [A]_0 e^{-k_A t} \tag{29}$$

Second Order

$$r = k[A]^2 \tag{30}$$

$$r = k[A][B] \tag{31}$$

Third Order

$$r = k[A]^3 \tag{32}$$

$$r = k[A]^2[B] \tag{33}$$

$$r = k[A][B][C] \tag{34}$$

Initial Rates of Reaction

The technique of initial rates of reaction is one common technique to determine the order of a reaction by keeping the concentration of one of more reactants fixed, while the concentration of one and only one of the reactants is varied and followed calorimetrically. Typically a graph of log T vs log [concentration] is drawn, and from the slopes of the fitted lines an order is obtained.

Constants and Conversion Factors

Energy

1 ev = 23.06035 kcal/mol
1 κT = 0.593 kcal/mol
1 hartree = 627.509 kcal/mol
1 hartree = 27.2116 eV
1 ev = 96.485 kJ/mol
1 ev = 1.602×10^{-19} J
1 hartree = 2624.5996 kJ/mol
1mh = 2625 kJ/mol
h = 6.6260755 x 10^{-34} J s
k_β = 1.380658 x 10^{-23} J/K
1 hartree = 4.3597482 x 10^{-18} J
1 kcal/mol = 4.184 J/mol

ZPVE (hartree)=
2.27817 x 10^{-6} * vib. wavenumber (cm^{-1})

Vibrational temperature (Tv)=
Tv(K)=1.43877 * vib. wavenumber (cm^{-1})

physisorption
$\approx$ 20kJ/mol = 4.708 kcal/mol

chemisorption
$\approx$ 200 kJ/mol = 47.801 kcal/mol

hydrogen bond
$\approx$ 0.8 - 167 kJ/mol = 0.2 - 40.0 kcal/mol

Others

e = 1.60217733 x 10^{-19} Coul
1 Debye = 3.336 x 10^{-30} Coul m
1 Bohr (ao)= 0.529177249 Å
1 Dalton = 1 amu = (1/N$_A$)g
N$_A$ = 6.0221367 x 10^{23}/mol
c = 2.99792458 x 10^{10} cm/s

Molecular Scale

Molecule	Mass	Residues
80S Ribosome	4.3MDa	
70S Ribosome	2.6MDa	
Ribo-Proteins	4.4 - 61.2 kDa	
aa3r_human	33.9kDa	326
β-PGM	24.2kDa	221
base-pair	1.0kDa	2
glucose	180.0Da	1
water	18.0Da	1

Molecular Energies

Molecule	Energy
G.C	X
A.U	X
A	X
G	X
U	X
C	X
T	X

Molecular Motion

Bond	Time (fs)	Wavenumber (cm^-1)
O-H	0.108	3600
N-H	0.102	3400
C-H	8.994	3000

Notes

$$dG = dA + d(pV) \tag{35}$$
$$dG = dA + pdV + V\,dp \tag{36}$$

So, for the case where pressure and volume are constant or their change is insignificant, then, one can assume that $dG = dA$.

$$G = \mu N \tag{37}$$

Therefore, the chemical potential μ is the same as Gibb's free energy per particle!.

References

[1] Ira N. Levine *Physical Chemistry*(Second Edition). Mc Graw Hill, 1983.

[2] Gerald S. Manning *Chemical Thermodynamics Class-notes.* Rutgers University, 2003.