

Formulas and Constants in Chemical Thermodynamics

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First Law

$$dE = dQ + dW \quad (1)$$

Second Law

$$dS \geq \frac{dq}{T} \quad (2)$$

Third Law

$$\lim_{T \rightarrow 0} (\Delta G - \Delta H) = 0 \quad (3)$$

$$\lim_{T \rightarrow 0} -T\Delta S = 0 \quad (4)$$

System of Constant Composition

$$U = Q + W \quad (5)$$

$$H = U + PV \quad (6)$$

$$A = U - TS \quad (7)$$

$$G = H - TS \quad (8)$$

Euler's Reciprocity Relation

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

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

Maxwell Relations

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

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

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

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

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

Gibbs Equations

$$dU = TdS - PdV \quad (9)$$

$$dH = TdS + VdP \quad (10)$$

$$dA = -SdT - PdV \quad (11)$$

$$dG = -SdT + VdP \quad (12)$$

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

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

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

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

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

Clausius-Clapeyron

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (24)$$

Van der Waals

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

Ideal Solutions

$$\mu_i = \mu_i^\circ + RT \ln \chi_i \quad (26)$$

Kinetic Theory of Gases

Ideal Monoatomic Gas

$$C_v = \frac{3}{2}R \quad (27)$$

$$C_p = \frac{5}{2}R \quad (28)$$

Rate Laws

First Order

$$\begin{aligned}\frac{d[A]}{dT} &= -k_A[A] \\ \int \frac{d[A]}{[A]} &= -k_A \\ \ln \frac{[A]}{[A]_0} &= -k_A(t_2 - t_1) \\ [A] &= [A]_0 e^{-k_A t}\end{aligned}\tag{29}$$

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 or 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 $\log [\text{concentration}]$ is drawn, and from the slopes of the fitted lines an order is obtained.

Constants and Conversion Factors

Energy

$1 \text{ ev} = 23.06035 \text{ kcal/mol}$
 $1 \kappa T = 0.593 \text{ kcal/mol}$
 $1 \text{ hartree} = 627.509 \text{ kcal/mol}$
 $1 \text{ hartree} = 27.2116 \text{ eV}$
 $1 \text{ ev} = 96.485 \text{ kJ/mol}$
 $1 \text{ ev} = 1.602 \times 10^{-19} \text{ J}$
 $1 \text{ hartree} = 2624.5996 \text{ kJ/mol}$
 $1 \text{ mJ} = 2625 \text{ kJ/mol}$
 $h = 6.6260755 \times 10^{-34} \text{ J s}$
 $k_B = 1.380658 \times 10^{-23} \text{ J/K}$
 $1 \text{ hartree} = 4.3597482 \times 10^{-18} \text{ J}$
 $1 \text{ kcal/mol} = 4.184 \text{ J/mol}$

$\text{ZPVE (hartree)} =$
 $2.27817 \times 10^{-6} * \text{vib. wavenumber (cm}^{-1}\text{)}$

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

physisorption
 $\approx 20 \text{ kJ/mol} = 4.708 \text{ kcal/mol}$

chemisorption
 $\approx 200 \text{ kJ/mol} = 47.801 \text{ kcal/mol}$

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

water-dimer hbond
 $\approx 3.5 \text{ kcal/mol}$

Others

$e = 1.60217733 \times 10^{-19} \text{ Coul}$
 $1 \text{ Debye} = 3.336 \times 10^{-30} \text{ Coul m}$
 $1 \text{ Bohr (ao)} = 0.529177249 \text{ \AA}$
 $1 \text{ Dalton} = 1 \text{ amu} = (1/N_A) \text{ g}$
 $N_A = 6.0221367 \times 10^{23}/\text{mol}$
 $c = 2.99792458 \times 10^{10} \text{ cm/s}$

Molecular Scale

Molecule	Mass	Residues
80S Ribosome	4.3 MDa	
70S Ribosome	2.6 MDa	
Ribo-Proteins	4.4 - 61.2 kDa	
aa3r_human	33.9 kDa	326
β -PGM	24.2 kDa	221
adrb2 (seq)	46.5 kDa	413
G α S (seq)	45.7 kDa	394
β -arrestin 2	46.1 kDa	409
mapk14	41.3 kDa	360
base-pair	1.0 kDa	2
glucose	180.0 Da	1
water	18.0 Da	1

Note: The values for adrb2 β -arrestin 2 and G α S are computed from their sequence using web.expasy.org

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

$$dG = dA + d(pV) \quad (35)$$

$$dG = dA + pdV + Vdp \quad (36)$$

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

$$G = \mu N \quad (37)$$

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

References

- [1] Ira N. Levine *Physical Chemistry*(Second Edition). McGraw Hill, 1983.
- [2] Gerald S. Manning *Chemical Thermodynamics Classnotes*. Rutgers University, 2003.