

Equations – P-Chem

Entropy/Free Energy

Internal Energy

$$A=C \text{ \& } B=C, \text{ then } A=B$$

$$U_{\text{univ}} = U_{\text{sys}} + U_{\text{surr}} = \text{constant}$$

0th Law of Thermodynamics

1st Law of Thermodynamics (*energy cannot be created/destroyed*)

Entropy

$$S = k \ln W \quad \text{Boltzmann entropy formula}$$

$$dS = \frac{\delta Q}{T}$$

$$\varepsilon = -\frac{w_{\text{cycle}}}{q_1} = 1 - \frac{|q_3|}{|q_1|} \quad \text{Carnot cycle efficiency where } q_{\text{cycle}} = q_1 + q_3 \text{ and } -q_{\text{cycle}} = w_{\text{cycle}}$$

$$\varepsilon = 1 - \frac{T_C}{T_H} < 1 = -\frac{|q_3|}{|q_1|} = \frac{T_C}{T_H} \quad ; \quad \frac{|q_3|}{T_C} + \frac{|q_1|}{T_H} = 0$$

$$\oint \frac{dq_{\text{reversible}}}{T} = 0 \quad ; \quad dS = \frac{dq_{\text{reversible}}}{T}$$

Reversible irreversible

$$\Delta S = \Delta S_{\text{surr}} \quad ; \quad \Delta S_{\text{surr}} = \frac{-p_f \Delta V}{T} \quad ; \quad \Delta S_{\text{tot}} = \Delta S_{\text{surr}} + \Delta S$$

Reversible Isothermal expansion

$$\Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \left(\frac{V_f}{V_i} \right) =$$

isochoric heating

$$nC_{V,m} \ln \frac{T_f}{T_i} =$$

isobaric heating

$$nC_{p,m} \ln \frac{T_f}{T_i}$$

Phase transition

$$\Delta S_{\text{vaporization}} = \frac{q_{\text{reversible}}}{T_b} = \frac{\Delta H_{\text{vaporization}}}{T_b}$$

(T_b = boiling temperature)

Trouton's rule $\approx 10.5R$

$$\Delta S_{\text{fusion}} = \frac{q_{\text{reversible}}}{T_f} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

(T_f = freezing temperature)

$$\text{General phase transition } \Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

Combined Entropy Equation

$$\Delta S_m = C_{p,m}(s) \ln \left(\frac{T_{\text{fus}}}{T_i} \right) + \Delta_{\text{fus}} H / T_{\text{fus}} + C_{p,m}(l) \ln \left(\frac{T_b}{T_{\text{fus}}} \right) + \Delta_{\text{vap}} H / T_b + C_{p,m}(g) \ln \left(\frac{T'}{T_b} \right) - nR \ln \left(\frac{p'}{p_b} \right)$$

$$S_m(T') = S_m(T_i) + \Delta S_m$$

$$S = n \Delta S_m = k \ln W$$

$C_{p,m} = aT^3$ Debye Law at very low temperatures

Thermochemistry

$$\Delta H^\ominus(T_2) = \Delta H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$$

$$\Delta_r U^\ominus = \Delta_r H^\ominus - (\Delta n_g) RT$$

for Perfect Gases

$$G(T,P) = G^\ominus(T,P^\ominus) + nRT \ln \left(\frac{P}{P^\ominus} \right)$$

Gibbs free energy at nonstandard pressure

$$Q = \prod_j a_j^{\nu_j} \quad ; \quad K = (\prod_j a_j^{\nu_j})_{\text{equilibrium}}$$

[Q rxn quotient; K equilibrium constant]

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

Relationship between ΔG and Q

$$\Delta G^\ominus = -RT \ln K$$

Relationship between ΔG and K (equilibrium)

$$\mu_i = \left(\frac{\delta G}{\delta n_i} \right)_{p,T,n_k > n_i}$$

Definition of chemical potential

$$\Delta_{\text{solv}} G_o = \frac{z_i^2 e^2 N_A}{8 \pi \epsilon_0 r} \left(\frac{1}{\epsilon_r} \right) \quad z_i \text{ charge of ion; } e \text{ elementary charge; } r \text{ radius; } \epsilon_r \text{ permittivity radius}$$

Free Energy

$$A = U - TS$$

$$G = H - TS = U + pV - TS$$

$$dw_{\max} = dU - TdS = dA$$

$$\left(\frac{\delta G}{\delta p}\right)_T = \left(\frac{\delta H}{\delta p}\right)_S = V; \quad \left(\frac{\delta A}{\delta V}\right)_T = \left(\frac{\delta U}{\delta V}\right)_S = -p$$

$$\left(\frac{\delta U}{\delta S}\right)_V = \left(\frac{\delta H}{\delta S}\right)_p = T; \quad \left(\frac{\delta A}{\delta T}\right)_V = \left(\frac{\delta G}{\delta T}\right)_p = -S$$

Maxwell's Relations

$$-\left(\frac{\delta p}{\delta S}\right)_V = \left(\frac{\delta T}{\delta V}\right)_S; \quad \left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

$$\left(\frac{\delta V}{\delta S}\right)_p = \left(\frac{\delta T}{\delta p}\right)_S; \quad -\left(\frac{\delta S}{\delta p}\right)_T = \left(\frac{\delta V}{\delta T}\right)_p$$

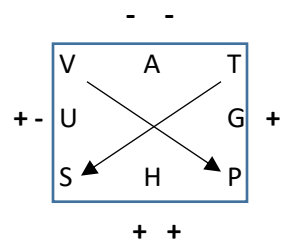
State Relationships

$$\Delta U = q + w \quad dU = TdS - pdV = \left(\frac{\delta U}{\delta S}\right)_V dS + \left(\frac{\delta U}{\delta V}\right)_S dV$$

$$H = U + pV = U + nRT \quad dH = TdS + Vdp = \left(\frac{\delta H}{\delta S}\right)_p dS + \left(\frac{\delta H}{\delta p}\right)_S dp$$

$$A = U - TS \quad dA = -SdT - pdV = \left(\frac{\delta A}{\delta T}\right)_V dT + \left(\frac{\delta A}{\delta V}\right)_T dV$$

$$G = H - TS \quad dG = -SdT + Vdp = \left(\frac{\delta G}{\delta T}\right)_p dT + \left(\frac{\delta G}{\delta p}\right)_T dp$$



Criteria of spontaneous change $dA_{T,V} \leq 0$ $dG_{T,p} \leq 0$

ΔH	ΔS	$-T\Delta S$	ΔG	Spontaneity
+	-	+	+	Nonspontaneous
-	+	-	-	Spontaneous
-	-	+	+ or -	Low Temp: Spontaneous High Temp: Nonspontaneous
+	+	-	+ or -	Low Temp: Nonspontaneous High Temp: Spontaneous

Chemical potential

$$d\mu = dG_m = -S_m dT + V_m dp = \left(\frac{d\mu}{dT}\right)_p dT + \left(\frac{d\mu}{dp}\right)_T dp$$

$$-S_m = \left(\frac{d\mu}{dT}\right)_p; \quad V_m = \left(\frac{d\mu}{dp}\right)_T$$

$$\Delta G_m = \int_{p_i}^{p_f} V_m dp$$

$$\sim V_m \Delta p \quad \text{solids/liquids}$$

$$= RT \ln\left(\frac{p_f}{p_i}\right) \quad \text{perfect gases}$$

$$G_m(p) = G_m^o + RT \ln\left(\frac{p}{p^o}\right)$$

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \therefore \Delta G(T_2) = \Delta G(T_1) \frac{T_2}{T_1} + \Delta H(T_1) \left(1 - \frac{T_2}{T_1}\right)$$

$$C_{p,m} = C_{v,m} + TV_m \left(\frac{\alpha^2}{\kappa_T}\right)$$

Phases and transitions

$$F = 3 - p \quad (F \text{ deg of freedom; } p = \text{phases}) \quad \text{Single substance}$$

$$F = C - p + 2 \quad (C \text{ \# components}) \quad \text{Generalized to more than one component substance}$$

$$\frac{dp}{dT} = \frac{\Delta_{trs} S_m}{\Delta_{trs} V_m} \quad \text{Clapeyron equation}$$

$$\left(\frac{\delta p}{\delta T}\right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \quad \text{solid-liquid coexistence curve}$$

$$\left(\frac{\delta p}{\delta T}\right)_{\text{vap}} = \frac{p \Delta H_{\text{vap}}}{RT^2} \quad - \text{ [Integrated form] } \ln \frac{p_f}{p_i} = - \frac{\Delta H_{\text{vap}}}{R} \times \left(\frac{1}{T_f} - \frac{1}{T_i}\right) \quad \text{Claisen-Clapeyron equation}$$

$$T_n = \left(\frac{1}{T_0} - \frac{R \ln\left(\frac{p_n}{p_0}\right)}{\Delta H_{\text{vap}}}\right)^{-1} \quad \text{subscripts: } n\text{-new, } o\text{-original} \quad \text{Change of boiling point w/ change pressure}$$

Important definitions for Perfect Gas

<u>Isothermal</u> process, constant temp:	$\Delta T = \Delta U = 0$;	$q = -w$
<u>Isochoric</u> process, constant volume:	$\Delta U = q$;	$w = 0$
<u>Isobaric</u> process, constant pressure:	$w = -p\Delta V$	
<u>Adiabatic</u> process, no heat exchange:	$\Delta U = w$;	$q = 0$

Constants

R = Gas constant = $N_A k$ (8.31446 J/Kmol or Pa m³/K mol) = 0.0831445 (dm³ bar /K mol)

= (0.0820574 dm³ atm /K mol) = (62.364 dm³ Torr/K mol) = (1.98721 cal/K mol)

C_s water = 4.184 ($\frac{J}{g K}$) = 1 $\frac{cal}{g K}$; C_m water = 75.4 ($\frac{J}{mol K}$); k = Boltzmann's constant (1.38065×10^{-23} J/K)

atm = 1.01325 bar = 101325 Pa = 760 torr ; bar = 1.0×10^5 Pa torr = mmHg = 133.322 Pa

Legend

d = distance, Collision diam	A = area, Helmholtz free energy	p = pressure (N/m ²)
V = volume	V_m = molar volume (V/n)	V_m^0 = molar vol of ideal gas
H = Enthalpy (J)	G = Gibbs free energy	A = Helmholtz free energy
U = Internal energy	w = work (J)	q = heat energy (J)
M = molar mass (Kg/mol)	F = force (N; Kg m/s ²)	n = moles (mol)
\mathcal{W} = number of microstates	N = total molecules	N_A = Avogadro's number
\mathcal{N} = number density (N/V)	E = Energy; electric field (J; N/C or V/m)	J = Joules (Nm or kg m ² /s ²)
π_T = Internal pressure ($\frac{J}{m^3}$)	α = expansion coefficient	\mathcal{K}_T = compressibility coefficient
H° = Std Enthalpy (J)	G° = Std Gibbs free energy	A° = Std Helmholtz free energy
$C_{V,s} = C_s$ = Specific Heat Capacity ($\frac{J}{<unit>K}$)	$C_{V,m} = C_m$ = Molar Heat Capacity, V	$C_{V,m}$ = Molar Heat Cap, const p
R = Gas constant = $N_A k$ (8.31446 J/Kmol)	k = Boltzmann's constant (1.38065×10^{-23} J/K)	