Equations in Thermodynamics and Kinetics **Chemistry BC3252**

$dU \equiv dq + dw$

pV work: $dw \equiv -p_{ex}dV$

Isothermal reversible expansion, ideal gas:

$w = -nRT \ln(V_2/V_1)$

$C_V \equiv (\partial U/\partial T)_V$

$C_p \equiv (\partial H/\partial T)_p$

Ideal gas: $C_p = C_V + nR$

Monatomic gas: $C_V = (3/2)R$

Reversible adiabatic expansion, ideal gas:

pV^γ and $VT^{Cv/nR}$ are constant $\gamma = C_p/C_V$

$dS \equiv dq_{rev}/T$

$H \equiv U + pV$

$A \equiv U - TS$

$G \equiv H - TS$

Inequality of Clausius: $(dq - TdS) \geq 0$

isolated: spontaneous if $\Delta S > 0$

fixed p, T: spontaneous if $\Delta G < 0$

Fundamental equations (n fixed)

$dU = +TdS - pdV$

$dH = +TdS + Vdp$

$dA = -SdT - pdV$

$dG = -SdT + Vdp$

Gibbs-Helmholtz equation

$[\partial(G/T)/\partial(1/T)]_p = H$ or

$[\partial(G/T)/\partial T]_p = -H/T^2$

$\mu_k \equiv (\partial G/\partial n_k)_{P,T,n'}$

For ideal gas: $\mu_k = \mu_k° + RT \ln p_k$

Fundamental equations (n varies)

$dU = + TdS - pdV + \sum \mu_k dn_k$

$dH = + TdS + Vdp + \sum \mu_k dn_k$

$dA = - SdT - pdV + \sum \mu_k dn_k$

$dG = - SdT + Vdp + \sum \mu_k dn_k$

Gibbs-Duhem equation:

$+ Vdp - SdT - \sum n_k d\mu_k = 0$

$Y_k \equiv (\partial Y/\partial n_k)_{p,T,n'}$ partial molar quantity

Additivity: $Y = \sum n_k Y_k$ e.g. $G = \sum n_k \mu_k$

Clapeyron Equation:

$dp/dT = \Delta S/\Delta V = \Delta H/T\Delta V$

Clausius-Clapeyron equation:

$d(\ln p)/d(1/T) = -\Delta H°/R$

$\ln(p_2/p_1) = -\Delta H°/R\{1/T_2 - 1/T_1\}$

$\Delta S_{mix} = -R \sum X_k \ln X_k$

$S = k_B \ln W$

Raoult's Law (ideal sol'n): $p_k = X_{k,\ell}\, p_k^*$

$\mu_k = \mu_k°^* + RT \ln X_k$ or

$\mu_k = \mu_k° + RT \ln [k]$

Gibbs phase rule: $f = 2 + c - p$

Reactions: $n_k = n_k° + \nu_k \xi$

ν_k = stoichiometric coefficient

$\Delta_r G \equiv \sum \mu_k \nu_k = (\partial G/\delta\xi)_p$

$\Delta_r G = \Delta_r G° + RT \ln Q$

for ideal gases $Q = \prod p_k^{\nu_k}$

$\Delta_r G° = -RT \ln K$ K = Q at equilibrium

In general: $\mu_k = \mu_k° + RT \ln a_k$

so $Q = \prod a_k^{\nu_k}$

Van't Hoff Equation:

$[\partial(\ln K)/\partial(1/T)]_p = -\Delta_r H°/R$ or

$[\partial(\ln K)/\partial T]_p = \Delta_r H°/RT^2$

1° kinetics: $c = c_0 e^{-kt}$ or $\ln c = \ln c_o - kt$

$t_{½} = (\ln 2)/k = 0.693/k$

2° kinetics: $1/[B] = 1/[B]_0 + kt$

$\ln([A]/[B]) = \ln([A]_0/[B]_0) + \{[A]_0 - [B\}_0\}kt$

Arrhenius equation: $k = A \exp(-E_a/RT)$

$k_{TST} = (k_B T/h) \exp(\Delta S^‡/R) \exp(-\Delta H^‡/RT)$