CHEMICAL THERMODYNAMICS
Formula Sheet
MAXWELL RELATIONS

\[ dU = Tds - Pdv \rightarrow \left( \frac{\partial T}{\partial V} \right)_s = -\left( \frac{\partial P}{\partial S} \right)_V \]

\[ dA = -SdT - Pdv \rightarrow \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \]

\[ dH = TdS + VdP \rightarrow \left( \frac{\partial T}{\partial P} \right)_s = \left( \frac{\partial V}{\partial S} \right)_P \]

\[ dG = -SdT + VdP \rightarrow -\left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P \]
THERMODYNAMIC VARIABLES

\[ S = -\left(\frac{dA}{dT}\right)_V = -\left(\frac{dG}{dT}\right)_P \]

\[ P = -\left(\frac{dU}{dV}\right)_S = -\left(\frac{dA}{dV}\right)_T \]

\[ V = \left(\frac{dH}{dP}\right)_S = \left(\frac{dG}{dP}\right)_T \]

\[ T = \left(\frac{dU}{dS}\right)_V = \left(\frac{dH}{dS}\right)_P \]

CRITERION OF SPONTANEITY

\[(dG)_{P,T} \leq 0\]
\[(dH)_{P,S} \leq 0 \text{ (not always)}\]
\[(dU)_{S,V} \leq 0\]
\[(dA)_{V,T} \leq 0\]

\[\Delta S \geq 0\]
\[\Delta S_{H,P} \geq 0\]
\[\Delta S_{U,V} \geq 0\]
FIRST LAW OF THERMODYNAMICS

Work of Compression/Expansion: \( W = -P \Delta V \)
Work done by the system= negative
Work done on the system= positive

\[ \Delta U = Q + W \]

Heat capacity, \( c = \frac{\Delta q}{\Delta T} \)

\[ \Delta U = nC_v\Delta T \]
\[ \Delta H = nC_P\Delta T \]
\[ \Delta H_2 - \Delta H_1 = nC_P(T_2 - T_1) \]

THERMODYNAMIC EQUATION OF STATE

1. \( \left( \frac{dU}{dV} \right)_T = T \left( \frac{dP}{dT} \right)_V - P \)  
   First T. Equation of state
   - For ideal gas, \( \left( \frac{dU}{dV} \right)_T = 0 \)
   - For real gas, \( \left( \frac{dU}{dV} \right)_T = \frac{a}{V^2} \)

2. \( \left( \frac{dH}{dP} \right)_T = -T \left( \frac{dV}{dT} \right)_P + V \)  
   Second T. Equation of state
   - For ideal gas, \( \left( \frac{dH}{dP} \right)_T = 0 \)
   - For real gas, \( \left( \frac{dH}{dP} \right)_T = \left( b - \frac{2a}{RT} \right) \)
RELATION BETWEEN $C_P$ and $C_V$

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

For van der Waals gas: $C_P - C_V = R \left( 1 + \frac{2a}{RTV} \right)$

TDS EQUATION

$$TdS = C_V dT + T \left( \frac{dP}{dT} \right)_V dV$$

So, $\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

$$TdS = C_p dT - T \left( \frac{dV}{dT} \right)_P dP$$

So, $\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$
THERMODYNAMIC COEFFICIENTS

1. \( \alpha = \left( \frac{dV}{V} \right)_T \), so, \( \alpha = \frac{1}{T} \)

2. \( \beta = \left( \frac{-dV}{V} \right)_P \), so, \( \beta = \frac{1}{P} \)

3. \( \gamma = \left( \frac{dP}{P} \right)_T \), so, \( \gamma = \frac{1}{T} \)

REVERSIBLE ISOTHERMAL PROCESS OF IDEAL GAS

\[ W = -2.303 \, nRT \log \frac{V_2}{V_1} \quad \text{or,} \quad W = -2.303 \, nRT \log \frac{P_1}{P_2} \]

IRREVERSIBLE ISOTHERMAL PROCESS OF IDEAL GAS

\[ W = -nRT \left( 1 - \frac{V_1}{V_2} \right) \]

- for isothermal process - \( W_{rev} > W_{irr} \)
REVERSIBLE ADIABATIC TRANSFORMATION OF IDEAL GAS

\[ W = \frac{nR}{\gamma - 1} (T_2 - T_1) \]

\[ W = \frac{1}{\gamma - 1} (P_2 V_2 - P_1 V_1) \]

And

\[ P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \]

\[ T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \]

for monoatomic gas - \( \gamma = 1.66 \)

for diatomic gas - \( \gamma = 1.4 \)

for triatomic/polyatomic gas - \( \gamma = 1.33 \)

IRREVERSIBLE ADIABATIC TRANSFORMATION OF IDEAL GAS

\[ nC_v(T_2 - T_1) = -nRT_2 \left( 1 - \frac{V_1}{V_2} \right) \]
(−W) isochoric > (−W) isothermal > (−W) adiabatic > (−W) isochoric

\[
\left(\frac{dP}{dV}\right)_{\text{adiabatic}} = \gamma \left(\frac{dP}{dV}\right)_{\text{isothermal}} \quad \text{where} \quad \gamma = \frac{C_p}{C_v}
\]

**enthalpy**

\[\Delta H = U + PV \quad \text{and} \quad \Delta H = Q_p\]

for isobaric process \(\rightarrow \Delta U = Q + W\)

So, \(\Delta (U + PV) = Q_p\)

**joule thomson effect**

\[-\frac{1}{C_p} \left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{dT}{dP}\right)_H\]

\[\text{So,} \quad \phi_{JT} = \left(\frac{\partial H}{\partial P}\right)_T \quad \text{and} \quad \mu_{JT} = \left(\frac{dT}{dP}\right)_H\]

**inversion temperature**

\[T_i = \frac{2a}{R_b} \quad \text{and} \quad T_i < T\]

**carnot engine**

\[W = -RT_h \ln \frac{V_2}{V_1} - RT_c \ln \frac{V_4}{V_3}\]

efficiency \(\eta = \frac{-W}{Q_h} = \frac{T_h - T_c}{T_h}\)

\[\eta_{\text{refrigerator}} = \frac{T_h}{T_h - T_c}\]
ENTROPY

\[ \Delta S = \frac{\Delta Q}{T} \quad \text{J/K} \]

\[ S = k \ln W \]

\[ S = k \ln [W(\mathcal{U}) \Delta E] \]

NERNST HEAT THEOREM (III law of Thermodynamics)

\[ \Delta S = 0 \]

\[ \lim_{T \to 0} \]

Change in ENTROPY for REVERSIBLE PHASE TRANSFORMATION

\[ \Delta S = \frac{\Delta Q}{T} = \frac{\Delta H_{\text{melting}}}{T} \]

\[ \Delta S = \frac{\Delta H_{\text{vaporisation}}}{T} \]

\[ \Delta S = \frac{\Delta H_{\text{sublimation}}}{T} \]
ENTROPY OF MIXING

\[ T_f = \frac{n_1 C_{p1} T_1 + n_2 C_{p2} T_2}{n_1 C_{p1} + n_2 C_{p2}} \]

\[ \Delta S_{\text{mix}} = -2.303 R \sum n_i \log x_i \]

GIBBS PARADOX

\[ \Delta S_{\text{mix}} = 0 \quad \text{and} \quad \Delta H_{\text{mix}} = 0 \]

RESIDUAL ENTROPY

\[ \Delta S = 0 \]

\[ \ln T \to 0 \]

\[ S = k \ln W \]
CLASSIUS CLAYPERON EQUATION

\[ \Delta S = \frac{\Delta H}{T} = \left( \frac{dP}{dT} \right) = \frac{\Delta H}{T \Delta V} \]

\[ \ln \frac{P_2}{P_1} = \frac{\Delta H}{nR} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \]

Dependence of G on P

\[ \Delta G_2 - \Delta G_1 = \Delta V (P_2 - P_1) \]

\[ \Delta G = nRT \ln \frac{P_2}{P_1} \]

For IDEAL GAS in ISOTHERMAL GAS

\[ \Delta G = nRT \ln \frac{V_1}{V_2} \]
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