## Formula Sheet *(Final Exam)*

*This formula sheet can be taken*
*home after the exam*

### Gas Laws (Ideal and Real Gases)

Ideal gas law:
$$PV = nRT$$

Compression factor:
$$Z = \frac{PV_m}{RT}$$

van der Waals equation:
$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Virial equation of state:
$$Z = \frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + ...$$

Law of corresponding states
$$\left(P_R + \frac{3}{V_{R,m}^2}\right)\left(V_{R,m} - \frac{1}{3}\right) = \frac{8}{3}RT_R$$

*where*
$$P_R = \frac{P}{P_C} \ ; \quad V_R = \frac{V}{V_C} \ ; \ T_R = \frac{T}{T_C}$$

### First Law of Thermodynamics

First law: $\Delta U = q + w$  *(where q and w are the heat transferred **to** the system and the work done **on** the system, respectively)*

Reversible $pV$ work:
$$w_{rev} = -\int_{V_1}^{V_2} PdV \ ; \qquad \delta w_{rev} = -PdV$$

Enthalpy (definition):
$$H = U + PV$$

Heat capacity at constant volume:
$$C_V = \frac{\delta q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

Heat capacity at constant pressure:
$$C_P = \frac{\delta q_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

For an ideal gas:
$$C_{P,m} = C_{V,m} + R$$

Ideal gas, reversible isothermal process: $\left(\frac{\partial U}{\partial V}\right)_T = 0$, and $w_{rev} = -q_{rev} = nRT \ln\frac{V_1}{V_2}$

Ideal gas, reversible adiabatic process: $P_i V_i^\gamma = P_f V_f^\gamma$ where $\gamma = \frac{C_P}{C_V}$

### Second Law of Thermodynamics

Carnot cycle, work and heat:
$$q_{cycle} = R(T_{hot} - T_{cold})\ln\frac{V_b}{V_a} = -w_{cycle}$$ *(per mole of ideal gas)*

Carnot cycle, thermodynamic efficiency: $\varepsilon \equiv \frac{-w_{cycle}}{q_{hot}} = 1 - \frac{T_{cold}}{T_{hot}}$

| Entropy (definition) | $\Delta S_{A \to B} = S_B - S_A \equiv \int_A^B \dfrac{\delta q_{rev}}{T}$ $or$ $dS \equiv \dfrac{\delta q_{rev}}{T}$ |
|---|---|

Second Law of Thermodynamics: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$ ;

Clausius inequality $dS \geq \dfrac{\delta q}{T}$

Ideal gas, entropy change: $\Delta S = n \int_{T_1}^{T_2} C_{V,m} \dfrac{dT}{T} + nR \ln \dfrac{V_2}{V_1}$

Ideal gas, molar entropy of mixing: $\Delta S_m = -R\left(x_1 \ln x_1 + x_2 \ln x_2\right)$

Entropy of fusion (melting): $\Delta S = \dfrac{q_{fus}}{T_{fus}} = \dfrac{\Delta H_{fus}}{T_{fus}}$ *(similar for other phase transitions)*

Joule-Thomson coefficient: $\mu_{J-T} = \left(\dfrac{\partial T}{\partial P}\right)_H$

## First and Second Laws Combined – Free Energies

Gibbs energy (definition) $G \equiv H - TS$ Helmholtz energy (definition) $A \equiv U - TS$

Process at const. T, V: spontaneous process if $dA < 0$; equilibrium if $dA = 0$

Process at const. T, p: spontaneous process if $dG < 0$; equilibrium if $dG = 0$

Gibbs equations: for $U = U(V,S)$: $dU = -PdV + TdS$

for $H = H(p,S)$: $dH = VdP + TdS$

for $A = A(V,T)$: $dA = -PdV - SdT$

for $G = G(p,T)$: $dG = VdP - SdT$

Maxwell's relations: $\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$ $\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$

$\left(\dfrac{\partial P}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$ $\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial S}{\partial P}\right)_T$

Gibbs-Helmholtz equation: $-\dfrac{\Delta H}{T^2} = \left[\dfrac{\partial}{\partial T}\left(\dfrac{\Delta G}{T}\right)\right]_P$

Thermochemistry – equilibrium constant: $\ln K = -\dfrac{\Delta G_R}{RT}$ Extent of reaction: $n_i(t) = n_i^{initial} + \nu_i \xi$

## Chemical Potential

Chemical potential of component i (definition) $\mu_i \equiv \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}$ *(similarly for multi-phase systems)*

Gibbs energy for an open system: $dG = -SdT + VdP + \sum_i \mu_i dn_i$ *(Gibbs equation)*

Material equilibrium condition: $\sum_i \mu_i dn_i = 0$

Phase equilibrium condition: $\mu_i^\beta = \mu_i^\delta$

## Phase Diagrams

Phase rule: $F = C - P + 2$

Clapeyron equation (differential form): $\dfrac{dP}{dT} = \dfrac{\Delta H_m}{T \Delta V_m}$ *(for a one-component system)*

Clausius-Clapeyron equation (differential form): $\dfrac{d \ln P}{dT} = \dfrac{\Delta H_m}{RT^2}$ *(if one phase corresponds to vapor)*

## Solutions

| | |
|---|---|
| Partial molar volume: | $\bar{V}_i \equiv \left(\dfrac{\partial V}{\partial n_i}\right)_{T,P,n_{j \neq i}}$ *(and similarly for any other extensive property)* |
| Solution volume: | $V = \sum_i n_i \bar{V}_i$ *(and similarly for any other extensive property)* |
| Ideal solutions: | $\mu_A = \mu_A^* + RT \ln x_A$ |
| Raoult's law: | $P_A = x_A P_A^*$      Henry's law: $P_j = x_j K_H^j$ |
| Activity; activity coeficient: | $a_i \equiv \dfrac{P_i}{P_i^*} \equiv \gamma_i x_i$ |
| Freezing point depression: | $\Delta T_{fus} = -\dfrac{R T_{fus}^{*2}}{\Delta H_{fus,m}} x_B$ |
| Boiling point elevation: | $\Delta T_{vap} = \dfrac{R T_{vap}^2}{\Delta H_{vap,m}} x_B$ |
| Osmotic pressure: | $\pi = \dfrac{RT}{V_{m,solvent}^*} x_B$   *(ideal solution)* |
| van't Hoff's equation: | $\pi = \dfrac{n_B}{V} RT$ |

## Electrochemistry

| | |
|---|---|
| Electrolyte solution: | $\mu_{\pm} = \dfrac{\mu_{solute}}{\nu} = \dfrac{\nu_+ \mu_+ + \nu_- \mu_-}{\nu}$    *where*    $\nu = \nu_+ + \nu_-$ |
| | $\mu_{\pm} = \mu_{\pm}^0 = RT \ln a_{\pm}$ |
| *where* | $a_{\pm}^{\nu} = a_+^{\nu_+} a_-^{\nu_-}$   (mean ionic activity) |

Cell potential $E$ and free energy of reaction:

$$\Delta G_R = -nFE \quad \text{(where n is the number of electrons.)}$$

Nernst equation:     $E = E^0 - \dfrac{RT}{nF} \ln Q$

*where* Q … reaction quotient
*with* $a_i$ … activities:     $a_i = \gamma_i x_i$

At chemical equilibrium: $Q = K$    and thus    $\ln K = \dfrac{nFE^0}{RT}$

## Units, Constants

Pressure:

$$Pa = kg\ m^{-1}\ s^{-2}$$

1 atm = 1.01325 x $10^5$ Pa;   1 Torr = 133.322 Pa;   1 bar = $10^5$ Pa

Energy:     $J = kg\ m^2\ s^{-2}$;    1 cal = 4.184 J

Temperature:     $T/K = \theta/{}^{o}C + 273.15$

Avogadro's number:     $N_0 = 6.0221367$ x $10^{23}$ mol$^{-1}$

Ideal gas constant:     $R = 8.3145101$ J mol$^{-1}$ K$^{-1}$ = 0.0820578 atm L K$^{-1}$ mol$^{-1}$

Faraday constant:     $F = N_0 e = 9.6485309$ x $10^4$ C mol$^{-1}$