**Equations, Units, and Tables**
**Final Exam**

First Law for closed systems:

$$dU + dE_{\mathrm{K}} + dE_{\mathrm{P}} = \delta Q + \delta W$$

$$\frac{dU}{dt} + \frac{dE_{\mathrm{K}}}{dt} + \frac{dE_{\mathrm{P}}}{dt} = \dot{Q} + \dot{W}$$

PV work:

$$\delta w_{\mathrm{m}} = -P_{\mathrm{E}} dv_{\mathrm{m}}$$

First Law for open systems with one input and one output stream:

$$\begin{aligned} dU + dE_{\mathrm{K}} + dE_{\mathrm{P}} = {} & dn_{\mathrm{in}}\left[h_{\mathrm{m}} + \frac{1}{2}|v|^2 (MW) + gz(MW)\right]_{\mathrm{in}} \\ & - dn_{\mathrm{out}}\left[h_{\mathrm{m}} + \frac{1}{2}|v|^2 (MW) + gz(MW)\right]_{\mathrm{out}} \\ & + \delta Q + \delta W_{\mathrm{s}} \end{aligned}$$

$$\begin{aligned} \frac{dU}{dt} + \frac{dE_{\mathrm{K}}}{dt} + \frac{dE_{\mathrm{P}}}{dt} = {} & \dot{n}_{\mathrm{in}}\left[h_{\mathrm{m}} + \frac{1}{2}|v|^2 (MW) + gz(MW)\right]_{\mathrm{in}} \\ & - \dot{n}_{\mathrm{out}}\left[h_{\mathrm{m}} + \frac{1}{2}|v|^2 (MW) + gz(MW)\right]_{\mathrm{out}} \\ & + \dot{Q} + \dot{W}_{\mathrm{s}} \end{aligned}$$

Thermodynamic property definitions:

$$h_{\mathrm{m}} = u_{\mathrm{m}} + Pv_{\mathrm{m}}$$
$$a_{\mathrm{m}} = u_{\mathrm{m}} - Ts_{\mathrm{m}}$$
$$g_{\mathrm{m}} = h_{\mathrm{m}} - Ts_{\mathrm{m}}$$

Enthalpy of vaporization:

$$\Delta h_{\mathrm{m,vap}}(T) = \Delta h_{\mathrm{m,vap}}(T_0) + \int_{T}^{T_0} c_{\mathrm{p,m}}^{\mathrm{liq}} dT + \int_{T_0}^{T} c_{\mathrm{p,m}}^{\mathrm{vap}} dT$$

Property data for ideal gases:

$$du_{\mathrm{m}} = c_{\mathrm{v,m}} dT$$
$$dh_{\mathrm{m}} = c_{\mathrm{p,m}} dT$$

Carnot efficiency:

$$\eta = \frac{T_{\mathrm{H}} - T_{\mathrm{C}}}{T_{\mathrm{H}}}$$

Entropy changes:

$$ds_{\mathrm{m}} = \frac{\delta q_{\mathrm{rev,m}}}{T}$$

Differential entropy change for an ideal gas:

$$ds_{\mathrm{m}} = c_{\mathrm{p,m}} \frac{dT}{T} - R\frac{dP}{P}$$

Second Law for closed systems:

$$\frac{dS}{dt} - \frac{\dot{Q}}{T_{\mathrm{surr}}} \geq 0$$

$$\Delta S - \frac{Q}{T_{\mathrm{surr}}} \geq 0$$

Second Law for open systems with one input and one output stream:

$$dS + s_{\mathrm{m,out}} dn_{\mathrm{out}} - s_{\mathrm{m,in}} dn_{\mathrm{in}} - \frac{\delta Q}{T_{\mathrm{surr}}} \geq 0$$

$$\frac{dS}{dt} + s_{\mathrm{m,out}} \dot{n}_{\mathrm{out}} - s_{\mathrm{m,in}} \dot{n}_{\mathrm{in}} - \frac{\dot{Q}}{T_{\mathrm{surr}}} \geq 0$$

Fundamental Equation of Thermodynamics (where only work is PV work or shaft work):

$$\begin{aligned} du_{\mathrm{m}} &= Tds_{\mathrm{m}} - Pdv_{\mathrm{m}} \\ dh_{\mathrm{m}} &= Tds_{\mathrm{m}} + v_{\mathrm{m}} dP \\ dg_{\mathrm{m}} &= -s_{\mathrm{m}} dT + v_{\mathrm{m}} dP \\ da_{\mathrm{m}} &= -s_{\mathrm{m}} dT - Pdv_{\mathrm{m}} \end{aligned}$$

Maxwell Relations (only work is PV work and shaft work):

$$\left(\frac{\partial T}{\partial v_{\mathrm{m}}}\right)_{s_{\mathrm{m}}} = -\left(\frac{\partial P}{\partial s_{\mathrm{m}}}\right)_{v_{\mathrm{m}}}$$

$$\left(\frac{\partial T}{\partial P}\right)_{s_{\mathrm{m}}} = \left(\frac{\partial v_{\mathrm{m}}}{\partial s_{\mathrm{m}}}\right)_{P}$$

$$\left(\frac{\partial s_{\mathrm{m}}}{\partial v_{\mathrm{m}}}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{v_{\mathrm{m}}}$$

$$-\left(\frac{\partial s_{\mathrm{m}}}{\partial P}\right)_{T} = \left(\frac{\partial v_{\mathrm{m}}}{\partial T}\right)_{P}$$

Selected real gas equations (others might need to be derived):

$$dh_{\mathrm{m}} = c_{\mathrm{p,m}} dT + \left[ v_{\mathrm{m}} - T\left(\frac{\partial v_{\mathrm{m}}}{\partial T}\right)_{P} \right] dP$$

$$du_{\mathrm{m}} = c_{\mathrm{v,m}} dT + \left[ T\left(\frac{\partial P}{\partial T}\right)_{v_{\mathrm{m}}} - P \right] dv_{\mathrm{m}}$$

$$ds_{\mathrm{m}} = \frac{c_{\mathrm{p,m}}}{T} dT - \left(\frac{\partial v_{\mathrm{m}}}{\partial T}\right)_{P} dP$$

$$ds_{\mathrm{m}} = \frac{c_{\mathrm{v,m}}}{T} dT + \left(\frac{\partial P}{\partial T}\right)_{v_{\mathrm{m}}} dv_{\mathrm{m}}$$

Cyclic rule (triple product rule):

$$-1 = \left(\frac{\partial x}{\partial z}\right)_{y} \left(\frac{\partial y}{\partial x}\right)_{z} \left(\frac{\partial z}{\partial y}\right)_{x}$$

Quotient rule:

$$\frac{d}{dx}\left[\frac{f(x)}{g(x)}\right] = \frac{g(x)f'(x) - f(x)g'(\mathrm{x})}{(g(x))^2}$$

Clapeyron equation:

$$\frac{dP}{dT} = \frac{h_m^{\alpha} - h_m^{\beta}}{T(v_m^{\alpha} - v_m^{\beta})}$$

Partial molar property definition:

$$\overline{K}_i = \left(\frac{\partial K}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Property changes of mixing:

$$\Delta K_{\mathrm{mix}} = K - \sum_i n_i k_{\mathrm{m},i} = \sum_i n_i (\bar{K}_i - k_{\mathrm{m},i})$$

$$\Delta k_{\mathrm{m,mix}} = k_{\mathrm{m}} - \sum_i x_i k_{\mathrm{m},i} = \sum_i x_i (\bar{K}_i - k_{\mathrm{m},i})$$

General form of the Gibbs–Duhem equation:

$$K = \sum_i \bar{K}_i n_i$$

$$0 = \left(\frac{\partial K}{\partial T}\right)_{P,n_1,\ldots n_m} dT + \left(\frac{\partial K}{\partial P}\right)_{T,n_1,\ldots n_m} dP - \sum_i n_i d\bar{K}_i$$

Fugacity equations for a pure component species:

$$d\mu = RTd\ln f = v_{\mathrm{m}} dP = -\left(\frac{\partial P}{\partial n}\right)_{T,V} dV$$

$$\phi = \frac{f}{P}$$

Fugacity equations for a species in a mixture:

$$d\mu_i = RTd\ln \hat{f}_i = \bar{V}_i dP = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} dV$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$$

Pure liquid fugacity:

$$f_i^{\mathrm{L}} = P_i^{\mathrm{sat}} \phi_i^{\mathrm{sat}} \exp\left[\frac{1}{RT}\int_{P_i^{\mathrm{sat}}}^{P} v_{\mathrm{m}}^{\mathrm{L}} dP\right]$$

Fugacities of species in a liquid mixture

$\hat{f}_i^{\mathrm{L}} = f_i^{\mathrm{L}} x_i \gamma_i$ for the Lewis–Randall reference state

$\hat{f}_i^{\mathrm{L}} = \mathrm{H}_i x_i \gamma_i^{\mathrm{H}}$ for the Henry's Law reference state

Lewis–Randall reference activity coefficients:

$$\bar{G}_i^{\mathrm{E}} = \left(\frac{\partial G^{\mathrm{E}}}{\partial n_i}\right)_{T,P,n_{j\neq i}} = RT\ln\gamma_i$$

Two-suffix Margules equation for a binary mixture:

$$g_{\mathrm{m}}^{\mathrm{E}} = A x_1 x_2$$

$$\gamma_1 = \exp\left[\frac{A}{RT} x_2^2\right] \qquad \gamma_2 = \exp\left[\frac{A}{RT} x_1^2\right]$$

Vapor–liquid equilibrium (VLE) equation:

$$P y_i \widehat{\phi}_i = f_i^{\mathrm{L}} x_i \gamma_i = \mathscr{H}_i x_i \gamma_i^{\mathrm{H}}$$

Raoult's Law (VLE with ideal vapor and ideal solution):

$$P y_i = P_i^{\mathrm{sat}} x_i$$

Total pressure of a VLE system:

$$P = \sum_i P_i = \sum_i y_i P$$

Azeotrope conditions:

$$y_i = x_i$$

Units and constants:

$R = 8.314$ J/(mol K) $\qquad g = 9.8$ m/s$^2$ $\qquad$ 1 bar = $10^5$ Pa = $10^5$ kg/(m s$^2$)