Equations, Units, and Tables
Midterm 2

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:

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

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

Enthalpy definition:

$$h_{\mathrm{m}} = u_{\mathrm{m}} + P v_{\mathrm{m}}$$

Heat capacity definitions:

$$c_{\mathrm{p,m}} = \left(\frac{\partial h_{\mathrm{m}}}{\partial T} \right)_P$$

$$c_{\mathrm{v,m}} = \left(\frac{\partial u_{\mathrm{m}}}{\partial T} \right)_{v_{\mathrm{m}}}$$

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)

$$du_{\mathrm{m}} = T ds_{\mathrm{m}} - P dv_{\mathrm{m}}$$
$$dh_{\mathrm{m}} = T ds_{\mathrm{m}} + v_{\mathrm{m}} dP$$
$$dg_{\mathrm{m}} = -s_{\mathrm{m}} dT + v_{\mathrm{m}} dP$$
$$da_{\mathrm{m}} = -s_{\mathrm{m}} dT - P dv_{\mathrm{m}}$$

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)

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

Clapeyron equation:

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

General form of the Gibbs–Duhem equation:

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

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

Units and constants:

$R = 8.314$ J/(mol K)

$g = 9.8$ m/s^2

1 bar = 10^5 Pa = 10^5 kg/(m s^2)

1 J = 1 kg m^2 s^{-2}

Equations that may or may not be needed.

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

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

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