Equation Sheet for Midterm 2

Compressibility Factor and Virial Equation of State

$$Z = \frac{V_{Real}}{V_{Ideal}} \qquad PV_{Real} = ZRT$$

$$PV_{Real} = ZRT = RT[1 + B'P + C'P^2 + D'P^3 + ...]$$

$$PV_{Real} = ZRT = RT[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + ...]$$

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2}, \quad D' = \frac{D - 3BC - 2B^3}{(RT)^3}$$

Reduced Variables, Corresponding States and Generalized Correlations

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c}$$

Table 3.1: Parameter Assignments for Equations of State

For use with Eqs. (3.49) through (3.56)

Eq. of State	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	Z_c
vdW (1873)	1	0	0	1/8	27/64	3/8
RK (1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
SRK (1972)	$\alpha_{SRK}(T_r;\omega)^\dagger$	1	0	0.08664	0.42748	1/3
PR (1976)	$\alpha_{PR}(T_r;\omega)^\ddagger$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

$^\dagger\alpha_{SRK}(T_r;\ \omega) = \left[1 + (0.480 + 1.574\,\omega - 0.176\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

$^\ddagger\alpha_{PR}(T_r;\ \omega) = \left[1 + (0.37464 + 1.54226\,\omega - 0.26992\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

Cubic Equations of State

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \text{(van der Waals EOS)}$$

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + \varepsilon b)(V + \sigma b)} \quad \text{(General Cubic EOS)}$$

$$a(T) = \Psi \frac{\alpha(T_r) R^2 T_C^2}{P_C}, \quad b = \Omega \frac{RT_C}{P_C}$$

Pitzer Correlations and Equations

$$Z = Z^0 + \omega Z^1, \quad Z^0 = 1 + B^0 \frac{P_r}{T_r}, \quad Z^1 = B^1 \frac{P_r}{T_r},$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

For saturated liquids

$$V^{sat} = V_C Z_C^{(1-T_r)^{2/7}}$$

Molar heat capacity

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + D/T^2$$

Entropy Equations and Second Law

$$\eta = 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{|T_c|}{|T_H|} \quad \text{(Carnot Efficiency)}$$

$$dS \equiv \left(\frac{\delta Q}{T}\right)_{rev}, \quad \oint\left(\frac{\delta Q}{T}\right)_{rev} = 0, \quad \oint\left(\frac{\delta Q}{T}\right)_{irrev} < 0$$

$$TdS = dH - VdP, \qquad TdS = dU + PdV$$

Derived equations

$$\frac{\Delta S}{R} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{R}\frac{dT}{T} - \ln\left(\frac{P_2}{P_1}\right) \quad \text{(ideal gas)}$$

$$\frac{\Delta S}{R} = \int_{T_1}^{T_2} \frac{C_p}{R}\frac{dT}{T} \quad \text{(solid or liquid, const. P)}$$

$$\Delta S = \frac{\Delta H_{transition}}{T_{Transition}} \quad \text{(phase change)}$$

$$\Delta S_{Total} = 0 \quad \text{(for a reversible process)}$$

$$\Delta S_{Total} > 0 \quad \text{(spontaneous, irreversible)}$$

Entropy Balance (note entropy is not conserved)

$$\frac{dS_{CV}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} + \Delta(\dot{m}S)_{fs} = \dot{S}_{gen} \geq 0$$

$$\Delta(\dot{m}S)_{fs} = \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} + \dot{S}_{gen} \quad \text{(steady state)}$$

Gibbs Equations and Maxwell's Equations

$$dU = TdS - PdV \qquad dH = TdS + VdP$$

$$dA = -PdV - SdT \qquad dG = VdP - SdT$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P,$$

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

Expressions Derived from Gibbs and Maxwell's

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$$ (fluids,const compn)

$$dS = \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dH = C_P dT + \left[V(1-\beta T\right]dP$$ (liquids)

$$dS = \frac{C_P}{T}dT - \beta V dP$$

$$dH^{ig} = C_P^{ig}dT$$ (ideal gases)

$$dS^{ig} = \frac{C_P^{ig}}{T}dT - \frac{R}{P}dP$$

Thermodynamic Properties of Fluids and Residual Properties

$$\frac{H}{RT} = -T\left[\frac{\partial\left(G/RT\right)}{\partial T}\right]_P \qquad \frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$

$H^R = H - H^{ig}$ $\quad S^R = S - S^{ig}$ $\quad V^R = V - V^{ig}$ etc ...

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(G^R/RT\right)}{\partial T}\right]_P \qquad \frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

$$\frac{G^R}{RT} = \int_0^P \frac{(Z-1)}{P}dP \quad , \frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \ ,$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P \frac{(Z-1)}{P}dP$$

Using Redlich-Kwong

$$\frac{H^R}{RT} = Z - 1 - \frac{7.4}{T_r^{1.5}}\ln\left(1 + \frac{0.08664P_r}{ZT_r}\right)$$

$$\frac{S^R}{R} = \ln\left(Z - \frac{0.08664P_r}{T_r}\right) - \frac{2.467}{T_r^{1.5}}\ln\left(1 + \frac{0.08664P_r}{ZT_r}\right)$$

Using Virial Equation and Pitzer Correlations

$$\frac{H^R}{RT_C} = P_r\left[B^0 - \frac{0.675}{T_r^{1.6}} + \omega\left(B^1 - \frac{0.722}{T_r^{4.2}}\right)\right]$$

$$\frac{S^R}{R} = -P_r\left[\frac{0.675}{T_r^{2.6}} + \omega\left(\frac{0.722}{T_r^{5.2}}\right)\right]$$

$$H = H_o^{ig} + \int_{T_o}^{T} C_p^{ig}dT + H^R$$

$$S = S_o^{ig} + \int_{T_o}^{T} \frac{C_p^{ig}}{T}dT - R\ln\left(\frac{P}{P_o}\right) + S^R$$

Where T_o and P_o are reference conditions where gas behaves ideally (e.g., $H^R = 0$ and $S^R = 0$)

Equation Sheet for Midterm 1 (for reference)

First Law General

$$dU = \partial Q + \partial W$$

ΔU^t = Q + W

$$W = -\int_{V_1}^{V_2} P_{ext} dV^t$$

$$\oint \delta Q_{cycle} = -\oint \delta W_{cycle}$$

where $\oint$ means to integrate around a cycle

H = U + PV

Phase Rule

F = 2 - π + N

Mass and Energy Balance

$$\frac{dm_{cv}}{dt} + \Delta(\rho A u) = 0$$

$$\Delta(\rho A u) = 0 \quad \text{(steady state)}$$

$$\frac{d\left(mU\right)_{cv}}{dt} = \dot{Q} + \dot{W} - \Delta\left[\left(H + \frac{u^2}{2} + zg\right)\dot{m}\right]_{fs}$$

$$\dot{Q} + \dot{W} = \Delta\left[\left(H + \frac{u^2}{2} + zg\right)\dot{m}\right]_{fs} \quad \text{(steady state)}$$

Ideal Gas

PV = RT dW = -P dV

$C_p = C_v + R$ $dU = C_V dT$ $dH = C_P dT$

$dQ = C_v dT + PdV$

$$dQ = C_V dT + RT\frac{dV}{V} \qquad dW = -RT\frac{dV}{V}$$

$$dQ = C_P dT - RT\frac{dP}{P} \qquad dW = -RdT + RT\frac{dP}{P}$$

$$dQ = \frac{C_V}{R} VdP + \frac{C_P}{R} PdV$$

Adiabatic (C$_P$ and C$_V$ must be constant with T)

$$P_1 V_1^\gamma = P_2 V_2^\gamma \qquad T_1 P_1^{\frac{1-\gamma}{\gamma}} = T_2 P_2^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

$$\gamma = \frac{C_P}{C_V} \qquad W = \frac{\left(P_2 V_2 - P_1 V_1\right)}{\gamma - 1}$$

Isothermal

$$Q = -W = RT \ln\frac{V_2}{V_1} = RT \ln\frac{P_1}{P_2}$$

Isobaric

$$Q = \Delta H = \int_1^2 C_P dT \qquad W = -R(T_2 - T_1)$$

Isochoric

$$Q = \Delta U = \int_1^2 C_V dT$$