CHEM E 325 Energy and Entropy

Thermodynamic Properties and Data

Description	Equations
Pressure (kinetic theory)	$P = \dfrac{F}{A}$
Ideal gas law	$PV = nRT$ $Pv = RT$
Quality	$q = \dfrac{n_v}{n_l + n_v}$
Fraction	$x_A = f^\alpha x_A^\alpha + (1 - f^\alpha) x_A^\beta$
Lever rule for intensive properties	$v_{\text{total}} = v_v q + v_l (1 - q)$
Gibbs phase rule	$\mathcal{F} = 2 + c - p - r$
Mole fraction	$x_i = \dfrac{n_i}{\sum_j n_j}$

Intermolecular Interactions

| Intermolecular potentials

Description	Equations
Keesom potential (dipole-dipole)	$\Gamma_{ij} = -\dfrac{2}{3} \dfrac{\mu_i^2 \mu_j^2}{r_{ij}^6 k_B T}$
Debye potential (dipole-induced dipole)	$\Gamma_{ij} = -\dfrac{\alpha_i \mu_j^2}{r_{ij}^6}$
London dispersion potential (induced dipole-induced dipole)	$\Gamma_{ij} = -\dfrac{3}{2} \dfrac{\alpha_i \alpha_j}{r_{ij}^6} \dfrac{1}{\frac{1}{I_i} + \frac{1}{I_j}}$
Lennard-Jones potential	$\Gamma = 4\varepsilon \left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^6 \right]$
Equilibrium intermolecular distance	$r(\Gamma_{\min}) = r(\varepsilon) = 2^{1/6} \sigma = 1.12\sigma$

| Molecular dynamics simulation

Description	Equations
Nondimensionalized distance	$\text{``}r\text{''} = \dfrac{r}{\sigma}$
Nondimensionalized temperature	$\text{``}T\text{''} = \dfrac{k_B T}{\varepsilon}$
Nondimensionalized pressure	$\text{``}P\text{''} = \dfrac{\sigma^3}{\varepsilon} P$
Nondimensionalized energy	$\text{``}E\text{''} = \dfrac{U}{\varepsilon}$
Nondimensionalized time	$\text{``}t\text{''} = \dfrac{t}{\sigma \sqrt{m/\varepsilon}}$
Kinetic energy and temperature	$\text{KE} = nT$
Ideal gas pair potential energy	$\text{PE} = 0$

Description	Equations
Condensed phase interaction potential energy (with normalized energy unit of ε)	$\mathrm{PE} = -N_{\mathrm{inter}}$
Amount of interactions	$N_{\mathrm{inter}} = \frac{1}{2}(\text{\# molecules})(\text{\# neighbors})$

Equation of States

| van der Waals EOS

Description	Equations
van der Waals EOS in terms of P	$P = \dfrac{RT}{v - b} - \dfrac{a}{v^2}$
van der Waals EOS in terms of v	$v^3 - \left(\dfrac{RT}{v - b}\right) v^2 + \dfrac{a}{P} v - \dfrac{a}{P} b = 0$
van der Waals parameter a	$a = \dfrac{27}{64} \dfrac{(RT_c)^2}{P_c}$
van der Waals parameter b	$b = \dfrac{RT_c}{8 P_c}$
Molar potential energy	$e_p = -\dfrac{a}{v}$
Pressure at zero kinetic energy	$P = -\dfrac{a}{v^2}$
Reduced temperature	$T_r = \dfrac{T}{T_c}$
Reduced pressure	$P_r = \dfrac{P}{P_c}$
Compressibility factor	$z = \dfrac{v_{\mathrm{real}}}{v_{\mathrm{ideal}}} = \dfrac{Pv}{RT}$
Potential energy	$e_p = u_{\mathrm{real}}(T, P) - u_{\mathrm{ideal}}(T, P = 0)$
Internal energy departure function	$\dfrac{e_p}{RT_c} = \dfrac{u_{\mathrm{real}} - u_{\mathrm{ideal}}}{RT_c}$
Internal energy departure function in van der Waals EOS	$\dfrac{e_p}{RT_c} = -\dfrac{27 P_r}{64 T_r z}$

| Lee-Kesler EOS

Description	Equations
Lee-Kesler compressibility factor	$z = z^{(0)} + \omega z^{(1)}$
Acentric factor	$\omega = -1 - \log_{10}(P_r^{\mathrm{sat}}(T_r = 0.7))$
General departure function in Lee-Kesler EOS	$\mathrm{dep} = \mathrm{dep}^{(0)} + \omega \, \mathrm{dep}^{(1)}$
Internal energy and enthalpy departure function	$\dfrac{u_{\mathrm{real}} - u_{\mathrm{ideal}}}{RT_c} = \dfrac{h_{\mathrm{real}} - h_{\mathrm{ideal}}}{RT_c} + T_r(1 - z)$

First Law of Thermodynamics

System Type	First Law of Thermodynamics
Isolated system	$\Delta U = 0$

System Type	First Law of Thermodynamics
Closed system	$\Delta U = Q + W$
Open system	$\dfrac{dU}{dt} = \sum\limits_{\text{in}} \dot{n}_i h_i - \sum\limits_{\text{out}} \dot{n}_i h_i + \sum \dot{Q}_i + \dot{W}_s$
Open system in steady state	$0 = \sum\limits_{\text{in}} \dot{n}_i h_i - \sum\limits_{\text{out}} \dot{n}_i h_i + \sum \dot{Q}_i + \dot{W}_s$

Description	Equations
Work	$W = \int P \, dV$
Enthalpy	$H = U + PV$
Constant volume molar heat capacity	$c_v = \left(\dfrac{\partial u}{\partial T} \right)_v$
Constant pressure molar heat capacity	$c_P = \left(\dfrac{\partial h}{\partial T} \right)_P$
Relationship between molar heat capacities	$c_P = c_v + R$

Second Law of Thermodynamics

System Type	Second Law of Thermodynamics
Isolated system $S_{\text{gen}} \geq 0$	$\Delta S = S_{\text{gen}}$
Closed system $S_{\text{gen}} \geq 0$	$\Delta S = \int \dfrac{\delta Q}{T} + S_{\text{gen}}$
Open system $\dot{S}_{\text{gen}} \geq 0$	$\dfrac{dS}{dt} = \sum\limits_{\text{in}} \dot{n}_i s_i - \sum\limits_{\text{out}} \dot{n}_i s_i + \sum \dfrac{\dot{Q}_i}{T_i} + \dot{S}_{\text{gen}}$
Open system in steady state $\dot{S}_{\text{gen}} \geq 0$	$0 = \sum\limits_{\text{in}} \dot{n}_i s_i - \sum\limits_{\text{out}} \dot{n}_i s_i + \sum \dfrac{\dot{Q}_i}{T_i} + \dot{S}_{\text{gen}}$

| Counting configurations

Description	Equations
Ergotic hypothesis	$|f| = \langle f \rangle$
Equal probability postulate	$P_j = \dfrac{1}{\Omega}$
Entropy	$S = k_B \ln \Omega$
Permutability N_A distinguishable particles in N sites	$\Pi = \dfrac{N!}{(N - N_A)!}$
Multiplicity N_A indistinguishable particles in N sites	$\Omega = \dfrac{N!}{N_A!(N - N_A)!}$
Multiplicity $N_A, N_B, \ldots$ indistinguishable particles in N sites	$\Omega = \dfrac{N!}{N_A! N_B! N_C! \cdots}$
Stirling approximation	$\lim\limits_{a \to \infty} \ln(a!) = a \ln(a) - a$
Entropy of N sites with fraction x activated	$S = k_B N[-x \ln(x) - (1 - x) \ln(1 - x)]$

Description	Equations
Molar entropy $\mathcal{C}$ = constant	$s = R\ln(vu^{3/2}) + \mathcal{C}$
Molar internal energy $\mathcal{C}$ = constant	$u = \mathcal{C}v^{-2/3}\exp\left(\dfrac{2}{3}\dfrac{s}{R}\right)$
Temperature	$T = \left(\dfrac{\partial u}{\partial s}\right)_v$
Pressure	$P = -\left(\dfrac{\partial u}{\partial v}\right)_s$
Fundamental property relation	$du = Tds - Pdv$
Reversible heat at constant v	$\Delta u = q = \int T\,ds$
Reversible work at constant s	$w = -\int P\,dv$

| **Entropy generation**

Description	Equations
Reversible process	$s_{\text{gen}} = 0$
Irreversible process (caused by temperature gradient)	$s_{\text{gen}} > 0$

First and Second Law Analysis

| **Isothermal/Isoenergetic process**

Isoenergetic process ($\Delta u = 0 \implies \Delta T = 0$) of ideal gas has similar analysis.

Description	Equations
Condition ★ Ideal gas	$\Delta T = 0$
Internal energy change	$\Delta u = 0$
Enthalpy change	$\Delta h = 0$
First law	$\Delta u = q + w = 0$
Work (changing volume)	$w = -\int \dfrac{RT}{v}dv = -RT\ln\left(\dfrac{v_2}{v_1}\right)$
Work (changing pressure)	$w = \int \dfrac{RT}{P}dP = RT\ln\left(\dfrac{P_2}{P_1}\right)$
Heat	$q = -w$
Entropy change	$\Delta s = \int \dfrac{\delta q}{T} = \dfrac{q}{T} = -\dfrac{w}{T}$
Entropy change (changing volume)	$\Delta s = R\ln\left(\dfrac{v_2}{v_1}\right)$
Entropy change (changing concentration)	$\Delta s = -R\ln\left(\dfrac{c_2}{c_1}\right)$

Description	Equations
Entropy change (changing pressure)	$\Delta s = -R \ln \left(\dfrac{P_2}{P_1} \right)$

| Adiabatic process

Description	Equations
Condition ★ Ideal gas	$q = 0$
First law	$\Delta u = w$
Enthalpy change	$\Delta h = \Delta u + R\Delta T$
Work (changing volume)	$w = -\displaystyle\int \dfrac{RT}{v} dv = -RT \ln \left(\dfrac{v_2}{v_1} \right)$
Work (changing pressure)	$w = \displaystyle\int \dfrac{RT}{P} dP = RT \ln \left(\dfrac{P_2}{P_1} \right)$
Entropy change	$\Delta s = 0$

| Isochoric process

Description	Equations
Condition ★ Ideal gas	$\Delta v = 0$
Work	$w = 0$
Internal energy change	$\Delta u = \displaystyle\int c_v \, dT$
First law	$q = \Delta u$
Entropy change	$\Delta s = \displaystyle\int \dfrac{\delta q}{T} = \int \dfrac{du}{T} = \int \dfrac{c_v}{T} \, dT$

| Isobaric process

Description	Equations
Condition ★ Ideal gas	$\Delta P = 0$
Internal energy change	$\Delta u = \displaystyle\int c_v \, dT$
Enthalpy change	$\Delta h = \displaystyle\int c_p \, dT$
Work	$w = -P\Delta v$
Heat	$q = \Delta h$
Entropy change	$\Delta s = \displaystyle\int \dfrac{\delta q}{T} = \int \dfrac{dh}{T} = \int \dfrac{c_p}{T} \, dT$

| Other processes

Description	Equations
Incompressible condensed phases	v_0 is constant, small
Incompressible condensed phases at low pressure	$\Delta u = \Delta h = \int c_p \, dT$
Incompressible condensed phases at high pressure	$\Delta h = \int c_p \, dT + v_0(P_1 - P_0)$
Incompressible condensed phases	$\Delta s = \int \frac{c_p}{T} dT = c_p \ln\left(\frac{T_1}{T_2}\right)$
Phase change	$\Delta h = q$ $\Delta s = \frac{q}{T} = \frac{\Delta h}{T}$

Process Efficiency

Description	Equations
Maximum work of heat engine	$W_{\mathrm{max}} = Q_{\mathrm{in}}\left(1 - \frac{T_c}{T_h}\right)$
Minimum work of heat heat pump	$W_{\mathrm{max}} = Q_{\mathrm{out}}\left(1 - \frac{T_c}{T_h}\right)$
Reversible work	$W_{\mathrm{rev}} = Q_1\left(1 - \frac{T_c}{T_h}\right)$
Carnot efficiency	$\eta = \frac{W_{\mathrm{rev}}}{Q_1} = 1 - \frac{T_c}{T_h}$
Ideal gas entropy	$\Delta s(T, v) = \int \frac{c_v}{T} dT + R \ln\left(\frac{v}{v_0}\right)$
Ideal gas entropy	$\Delta s(T, P) = \int \frac{c_p}{T} dT - R \ln\left(\frac{P}{P_0}\right)$
Lost work	$W_{\mathrm{lost}} = T_c s_{\mathrm{gen}}$
Exthalpy for multi-stream	$\dot{E} = \dot{W}_{\mathrm{rev}}$ $= \overset{\text{source}}{\underset{i}{\sum}} \dot{n}_i(h_i - T_0 s_i) - \overset{\text{ground}}{\underset{i}{\sum}} \dot{n}_i(h_i^\circ - T_0 s_i^\circ)$
Exthalpy for single stream	$\dot{W}_{\mathrm{rev}} = \Delta h - T_0 \Delta s$

Phase equilibrium

| Single component equilibrium

Description	Equations
Gibbs free energy (constant T, P)	$G = H - TS$
Helmholtz free energy (constant T, V)	$F = A = U - TS$
Entropy change of universe	$\Delta S_{\mathrm{univ}} \geq 0$
Gibbs free energy change of spontaneous process	$\Delta G \leq 0$
Helmholtz free energy change of spontaneous process	$\Delta F \leq 0$
Thermal equilibrium	$T^\alpha = T^\beta$
Mechanical equilibrium	$P^\alpha = P^\beta$

Description	Equations
Chemical equilibrium	$g^\alpha = g^\beta$
Clausius-Clapeyron equation	$\dfrac{d \ln P_{\text{sat}}}{d(1/T)} = -\dfrac{1}{R}\Delta h_{\text{vap}}(T)$
Clausius-Clapeyron equation ★ modest pressure, incompressible liquid, ideal gas, constant Δh_{vap}	$\ln\left(\dfrac{P_{\text{sat}}}{P_0}\right) = -\dfrac{\Delta h^\circ_{\text{vap}}}{R}\left(\dfrac{1}{T} - \dfrac{1}{T_0}\right)$
Antoine equation	$\ln(P_{\text{sat}}) = A - \dfrac{B}{C + T}$

| Multicomponent equilibrium

Description	Equations
Partial molar properties	$\bar{x}_i = \left(\dfrac{\partial x}{\partial n_i}\right)_{\text{others},nj\neq i}$
Partial molar gibbs free energy	$\bar{g}_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,nj\neq i}$
Partial molar gibbs free energy	$\bar{g}_i = \bar{h}_i - T\bar{s}_i$
Entropy	$S = -\left(\dfrac{\partial G}{\partial T}\right)_{P,nj}$
Volume	$V = \left(\dfrac{\partial G}{\partial P}\right)_{T,nj}$
Total derivative of gibbs free energy	$dG = -S\,dT + V\,dP + \sum_i \bar{g}_i\,dn_i$
Chemical potential	$\mu_i = \bar{g}_i$
Chemical equilibrium	$\mu_i^\alpha = \mu_i^\beta$
Raoult's law	$P_A = x_A^g P = x_A^l P_A^{\text{sat}}$
Condensation curve	$P = (P_A^{\text{sat}} - P_B^{\text{sat}})x_A^l + P_B^{\text{sat}}$
Boiling curve	$P = \dfrac{P_A^{\text{sat}} P_B^{\text{sat}}}{P_A^{\text{sat}} - (P_A^{\text{sat}} - P_B^{\text{sat}})x_A^g}$
Henry's law ★ Low pressure, dilute solution	$C_A = K_H(T)P_A$
Gibbs-Duhem Equations	$\sum \mu_i\,dn_i = 0$ $\sum n_i\,d\mu_i = 0$
Colligative property	$\mu_{\text{solvent}} = RT\ln(1 - x_A) + \mu^\circ_{\text{solvent}}$