

6. How is the internal energy of a substance related to the intermolecular pair potentials of the molecules?
7. Are T and P intensive properties? Name two intensive properties and two extensive properties.
8. How many degrees of freedom exist when a pure substance coexists as a liquid and gas?
9. Can an ideal gas condense? Can real fluids that follow the ideal gas law condense?
10. Give examples of bubble, dew, saturation, and superheated conditions. Explain what is meant when wet steam has a quality of 25%.
11. Create and solve a problem that requires double interpolation.

1.6 HOMEWORK PROBLEMS

Note: Some of the steam table homework problems involve enthalpy, H , which is defined for convenience using properties discussed in this chapter, $H \equiv U + PV$. The enthalpy calculations can be performed by reading the tabulated enthalpy values from the tables in an analogous manner used for internal energy.

- 1.1 In each of the following, sketch your estimates of the intermolecular potentials between the given molecules and their mixture on the same pair of axes.
 - (a) Chloroform is about 20% larger than acetone and about 10% stickier, but chloroform and acetone stick to each other much more strongly than they stick to themselves.
 - (b) You have probably heard that “oil and water don’t mix.” What does that mean in molecular terms? Let’s assume that oil can be characterized as benzene and that benzene is four times larger than water, but water is 10% stickier than benzene. If the ϵ_{12} parameter is practically zero, that would represent that the benzene and water stick to themselves more strongly than to each other. Sketch this.
- 1.2 For each of the states below, calculate the number of moles of ideal gas held in a three liter container.
 - (a) $T = 673 \text{ K}$, $P = 2 \text{ MPa}$
 - (b) $T = 500 \text{ K}$, $P = 0.7 \text{ MPa}$
 - (c) $T = 450 \text{ K}$, $P = 1.5 \text{ MPa}$
- 1.3 A 5 m^3 tank farm gas storage tank contains methane. The initial temperature and pressure are $P = 1 \text{ bar}$, $T = 18^\circ\text{C}$. Calculate the P following each of the successive steps using the ideal gas law.
 - (a) 1 m^3 (at standard conditions) is withdrawn isothermally.
 - (b) The sun warms the tank to 40°C .
 - (c) 1.2 m^3 (at standard conditions) is added to the tank and the final temperature is 35°C .
 - (d) The tank cools overnight to 18°C .
- 1.4 A 5 m^3 outdoor gas storage tank warms from 10°C to 40°C on a sunny day. If the initial pressure was 0.12 MPa at 10°C , what is the pressure at 40°C , and how many moles of gas are in the tank? Use the ideal gas law.
- 1.5 An automobile tire has a pressure of 255 kPa (gauge) in the summer when the tire temperature after driving is 50°C . What is the wintertime pressure of the same tire at 0°C if the volume of the tire is considered the same and there are no leaks in the tire?

2.19 HOMEWORK PROBLEMS

- 2.1 Five grams of the specified pure solvent is placed in a variable volume piston. What are the molar enthalpy and total enthalpy of the pure system when 50% and 75% have been evaporated at: (i) 30°C, (ii) 50°C? Use liquid at 25°C as a reference state.
- benzene ($\rho^L = 0.88 \text{ g/cm}^3$)
 - ethanol ($\rho^L = 0.79 \text{ g/cm}^3$)
 - water without using the steam tables ($\rho^L = 1 \text{ g/cm}^3$)
 - water using the steam tables
- 2.2 Create a table of T , U , H for the specified solvent using a reference state of $H = 0$ for liquid at 25°C and 1 bar. Calculate the table for: (i) liquid at 25°C and 1 bar; (ii) saturated liquid at 1 bar; saturated vapor at 1 bar; (iii) vapor at 110°C and 1 bar. Use the Antoine Equation (Appendix E) to relate the saturation temperature and saturation pressure. Use the ideal gas law to model the vapor phase.
- benzene
 - ethanol
 - water without using the steam tables
 - water using the steam tables
- 2.3 Three moles of an ideal gas (with temperature-independent $C_p = (7/2)R$, $C_v = (5/2)R$) is contained in a horizontal piston/cylinder arrangement. The piston has an area of 0.1 m^2 and mass of 500 g. The initial pressure in the piston is 101 kPa. Determine the heat that must be extracted to cool the gas from 375°C to 275°C at: (a) constant pressure; (b) constant volume.
- 2.4 One mole of an ideal gas ($C_p = 7R/2$) in a closed piston/cylinder is compressed from $T^i = 100 \text{ K}$, $P^i = 0.1 \text{ MPa}$ to $P^f = 0.7 \text{ MPa}$ by the following pathways. For each pathway, calculate ΔU , ΔH , Q , and W_{EC} : (a) isothermal; (b) constant volume; (c) adiabatic.
- 2.5 One mole of an ideal gas ($C_p = 5R/2$) in a closed piston/cylinder is compressed from $T^i = 298 \text{ K}$, $P^i = 0.1 \text{ MPa}$ to $P^f = 0.25 \text{ MPa}$ by the following pathways. For each pathway, calculate ΔU , ΔH , Q , and W_{EC} : (a) isothermal; (b) constant volume; (c) adiabatic.
- 2.6 One mole of an ideal gas ($C_p = 7R/2$) in a closed piston/cylinder is expanded from $T^i = 700 \text{ K}$, $P^i = 0.75 \text{ MPa}$ to $P^f = 0.1 \text{ MPa}$ by the following pathways. For each pathway, calculate ΔU , ΔH , Q , and W_{EC} : (a) isothermal; (b) constant volume; (c) adiabatic.
- 2.7 One mole of an ideal gas ($C_p = 5R/2$) in a closed piston/cylinder is expanded from $T^i = 500 \text{ K}$, $P^i = 0.6 \text{ MPa}$ to $P^f = 0.1 \text{ MPa}$ by the following pathways. For each pathway, calculate ΔU , ΔH , Q , and W_{EC} : (a) isothermal; (b) constant volume; (c) adiabatic.
- 2.8 (a) What is the enthalpy change needed to change 3 kg of liquid water at 0°C to steam at 0.1 MPa and 150°C?
 (b) What is the enthalpy change needed to heat 3 kg of water from 0.4 MPa and 0°C to steam at 0.1 MPa and 150°C?
 (c) What is the enthalpy change needed to heat 1 kg of water at 0.4 MPa and 4°C to steam at 150°C and 0.4 MPa?
 (d) What is the enthalpy change needed to change 1 kg of water of a water-steam mixture of 60% quality to one of 80% quality if the mixture is at 150°C?

80%; the feedwater leaving the closed preheater is 5°C below the temperature of the condensate draining from the bottom of the closed preheater. For the options below, calculate:

- the flowrate of stream 1;
- the thermal efficiency of the plant;
- the size of the feedwater pump (kW).

Options:

- $T_1 = 500^\circ\text{C}$, $P_1 = 4 \text{ MPa}$, $P_2 = 0.8 \text{ MPa}$, $T_{3a} = 500^\circ\text{C}$, $P_4 = 0.01 \text{ MPa}$.
- $T_1 = 600^\circ\text{C}$, $P_1 = 4 \text{ MPa}$, $P_2 = 1.2 \text{ MPa}$, $T_{3a} = 600^\circ\text{C}$, $P_4 = 0.01 \text{ MPa}$.

4.5 A regenerative Rankine cycle utilized the schematic of Fig. 4.7 on page 148. Conditions are: stream 1, 450°C, 3 MPa; stream 2, 250°C, 0.4 MPa; stream 3, 150°C, 0.1 MPa; stream 4, 0.01 MPa; stream 9, 140°C, $H = 592 \text{ kJ/kg}$.

- Determine the pressures for streams 5,6,8,9,10.
- Determine \dot{m}_2/\dot{m}_1 .
- Determine the enthalpies of streams 5 and 6 if the pump is 80% efficient.
- Determine the efficiency of turbine stage I.
- Determine the output of turbine stage III per kg of stream 4 if the turbine is 80% efficient.
- Determine \dot{m}_3/\dot{m}_1 .
- Determine the work output of the system per kg of stream 1 circulated.

4.6 A regenerative Rankine cycle uses one open feedwater preheater and one closed feedwater preheater. Using the stream numbering from Fig. 4.7 on page 148, and the specified conditions below, the plant capacity is to be 75 MW. Other constraints are: the efficiency of each turbine stage is 85%; the pump efficiencies are 80%; the feedwater leaving the closed preheater is 5°C below the temperature of the condensate draining from the bottom of the closed preheater. For the options below, calculate:

- the flowrate of stream 1;
- the thermal efficiency of the plant;
- the size of the feedwater pumps (kW);
- and the overall efficiency of the multistage turbine.

Options:

- the conditions are: $T_1 = 500^\circ\text{C}$, $P_1 = 4 \text{ MPa}$, $P_2 = 0.7 \text{ MPa}$, $P_3 = 0.12 \text{ MPa}$, $P_4 = 0.02 \text{ MPa}$.
- the conditions are: $T_1 = 600^\circ\text{C}$, $P_1 = 4 \text{ MPa}$, $P_2 = 1.6 \text{ MPa}$, $P_3 = 0.8 \text{ MPa}$, $P_4 = 0.01 \text{ MPa}$.

4.7 A regenerative Rankine cycle uses three closed feedwater preheaters. Using the stream numbering from Fig. 4.5 on page 147, and the specified conditions below, the plant capacity is to be 80 MW. Other constraints are: the efficiency of each turbine stage is 88%; the pump efficiency is 80%; the feedwater leaving each preheater is 5°C below the temperature of the condensate draining from the bottom of each preheater. For the options below, calculate:

- the flowrate of stream 1;
- the thermal efficiency of the plant;
- and the size of the feedwater pump (kW).

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- (c) The heat capacity at constant force is given by

$$C_F = T \left(\frac{\partial S}{\partial T} \right)_F$$

Derive a relation for $C_F - C_L$ and show whether this difference is positive, negative, or zero.

- (d) The same amount of heat flows into two rubber bands, but one is held at constant tension and the other at constant length. Which has the largest increase in temperature?
- (e) Show that the dependence of $k(T)$ on temperature at constant length is related to the dependence of entropy on length at constant temperature. Offer a physical description for the signs of the derivatives.

5.10 Express the following in terms of U , H , S , G , and their derivatives.

$$\left(\frac{\partial(A/RT)}{\partial T} \right)_V$$

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7.14 N.B. Vargaftik¹ (1975) lists the following experimental values for the enthalpy departure of isobutane at 175°C. Compute theoretical values and their percent deviations from experiment by

- (a) the generalized charts
- (b) the Peng-Robinson equation

Table 7.1 Enthalpy departure of isobutane at 175°C

P (atm)	10	20	35	70
$H-H^{ig}$ (J/g)	-15.4	-32.8	-64.72	-177.5

7.15 n -pentane is to be heated from liquid at 298 K and 0.01013 MPa to vapor at 360 K and 0.3 MPa. Compute the change in enthalpy using the Peng-Robinson equation of state. If a reference state is desired, use vapor at 310 K, 0.103 MPa, and provide the enthalpy departure at the reference state.

7.16 For each of the fluid state changes below, perform the following calculations using the Peng-Robinson equation: (a) prepare a table and summarize the molar volume, enthalpy, entropy for the initial and final states; (b) calculate ΔH and ΔS for the process; (c) compare with ΔH and ΔS for the fluid modeled as an ideal gas. Specify your reference states.

- (i) Propane vapor at 1 bar and 60°C is compressed to a state of 125 bar and 250°C.
- (ii) Methane vapor at -40°C and 0.1013 MPa is compressed to a state of 10°C and 7 MPa.

7.17 1 m³ of CO₂ initially at 150°C and 50 bar is to be isothermally compressed in a frictionless piston/cylinder device to a final pressure of 300 bar. Calculate the volume of the compressed gas, $\Delta \underline{U}$, the work done to compress the gas, and the heat flow on compression assuming:

- (a) CO₂ is an ideal gas
- (b) CO₂ obeys the Peng-Robinson equation of state

7.18 Solve problem 7.17 for an adiabatic compression.

7.19 Consider problem statement 2.29 using benzene as the fluid rather than air and eliminating the ideal gas assumption. Use the Peng-Robinson equation. For the same initial state,

- (a) The final tank temperature will not be 499.6 K. What will the temperature be?
- (b) What is the number of moles left in the tank at the end of the process?
- (c) Write and simplify the energy balance for the process. Determine the final temperature of the piston/cylinder gas.

7.20 Solve problem 7.19 using n -pentane.

1. See Vargaftik reference homework problem 6.6.

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$$\left(\frac{\partial G^L}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial G^V}{\partial n_2}\right)_{T,P,n_1}; \quad x_2 = 1 - x_1; \quad y_2 = 1 - y_1; \quad \text{which gives 4 equations with 4 unknowns}$$

(x_1, x_2, y_1, y_2) that we can solve, in principle.¹ The first two equations are simply the equivalency of chemical potentials in the two phases.

Chemical Potential of a Pure Fluid

In Chapter 8, we showed the equilibrium constraint for a pure fluid is equality of the molar Gibbs energy in each the phases (*c.f.* Eqn. 8.3). How does this relate to Eqn. 9.10?

$$\mu_i \equiv (\partial(nG) / \partial n_i)_{T,P} = G(\partial n / \partial n_i)_{T,P} + n(\partial G / \partial n_i)_{T,P}$$

For a pure fluid, there is only one component, so $dn_i = dn$, and since $G(T,P)$ is intensive, then $n(\partial G / \partial n)_{T,P} = 0$. Also $(\partial n / \partial n_i)_{T,P} = 1$ by Eqn. 5.13. Therefore,

$$\mu_{i,pure} = G \quad 9.11$$

! The chemical potential of a pure fluid is simply the molar Gibbs energy.

That is, the chemical potential of a pure fluid is simply the molar Gibbs energy. Pure components can be considered as a special case of the same general statement of the equilibrium constraint.

Fugacity

We introduced fugacity in the last chapter. The chemical potential constraint is sufficient for solving any phase equilibrium problem, but the most popular approach for actual computations makes use of the concept of fugacity. Fugacity is basically a quantity that has come to be recognized as more “user-friendly” than “chemical potential” or “partial molar Gibbs energy.” It may not sound user-friendly, but it makes sense if one studies the roots of the term. Fuga- comes from a root referring to flight. The suffix -ity comes from a root meaning “character.” Thus, fugacity was invented to mean flight-character, commonly called “escaping tendency” and is best thought of relative to liquid solutions. In an equimolar liquid solution, the component with the higher fugacity (“escaping tendency”) will be more prevalent in the vapor phase.²

We note that the chemical potential is applicable to pure fluids as well as to components in mixtures. Therefore, let us generalize our pure component relations to become relations for components in mixtures: at constant T , we defined $RT d \ln f \equiv dG$ (Eqn. 8.19) which can be generalized to mixtures as

$$RT d \ln \hat{f}_i \equiv d\mu_i \quad 9.12$$

where \hat{f}_i is the fugacity of component i in a mixture and μ_i is the chemical potential of the component. In the limit as the composition approaches a pure composition, these properties become

! Fugacity is another way to express the chemical potential that is used more widely in engineering than chemical potential.

1. Even though $\mu^L = \mu^V$ at equilibrium, the dependency of μ^V on composition will be quite different from the dependency of μ^L on composition because the molecules are arranged very differently.

2. The concept of fugacity becomes useful when we begin to discuss phase equilibrium in mixtures. In that case, it is conceivable that we could have some supercritical component dissolved in the liquid phase despite its high escaping tendency, (e.g. CO₂ in soda pop at 100°F). The possibility of a component that cannot be a liquid still dissolving in a liquid requires a very general concept of escaping tendency because the pure-component vapor pressure does not exist at those conditions. The definition of fugacity provides us with that general concept.

These equations may be used for bubble or dew-pressure calculations without iterations. For bubble or dew-point temperatures, iteration is required. A first guess may be obtained from one of the following formulas:

$$T = \sum_i x_i T_i^{sat}$$

$$T = \frac{\sum_i y_i T_{r,i} T_i^{sat}}{\sum_i y_i T_{c,i}} \quad 9.62$$

But these are somewhat inaccurate guesses which require subsequent iteration.¹

For isothermal flash calculations, the general formula is:

$$\sum_i x_i - \sum_i y_i = \sum_i \frac{z_i(1 - K_i)}{K_i + (L/F)(1 - K_i)} \equiv \sum_i D_i = 0 \quad 9.63$$

Iterative Calculations by Excel

The Solver tool in Excel is useful for performing iterative calculations. Many of the following examples summarize detailed calculations to illustrate fully the iterative procedure. In practice, the detailed calculations can be performed rapidly on a spreadsheet. Appendix A summarizes the use of Solver and the methods for successive substitution.

Example 9.1 Bubble and dew temperatures and isothermal flash of ideal solutions

The overhead from a distillation column is to have the following composition:

	$z(\text{Overhead})$
Propane	0.23
Isobutane	0.67
<i>n</i> -Butane	0.10
Total	1.00

1. Note that Eqns. 9.60–9.62 can be used to estimate the bubble and dew points regardless of whether the components are supercritical or whether vapor and liquid phases are indeed possible. We will see in the discussion of equations of state that mixtures can have critical points, too, and this leads to a number of subtle complexities.

9.9 PRACTICE PROBLEMS

- P9.1 The stream from a gas well consists of 90 mol% methane, 5 mol% ethane, 3 mol% propane, and 2 mol% *n*-butane. This stream is flashed isothermally at 233 K and 70 bar. Use the shortcut *K*-ratio method to estimate the *L/F* fraction and liquid and vapor compositions. (ANS. $L/F = 0.181$)
- P9.2 An equimolar mixture of *n*-butane and *n*-hexane at pressure *P* is isothermally flashed at 373 K. The liquid-to-feed ratio is 0.35. Use the shortcut *K*-ratio method to estimate the pressure and liquid and vapor compositions. (ANS. $P = 0.533$ MPa, $x_{C6} = 0.78$)
- P9.3 A mixture of 25 mol% *n*-pentane, 45 mol% *n*-hexane, and 30 mol% *n*-heptane is flashed isothermally at 365.9 K and 2 bar. Use the shortcut *K*-ratio method to estimate the *L/F* fraction and liquid and vapor compositions. (ANS. $L/F = 0.56$)
- P9.4 A mixture containing 15 mol% ethane, 35 mol% propane, and 50 mole% *n*-butane is isothermally flashed at 9 bar and temperature *T*. The liquid-to-feed ratio is 0.35. Use the shortcut *K*-ratio method to estimate the pressure and liquid and vapor compositions. (ANS. 319.4 K, $x_{C4} = 0.74$)

9.10 HOMEWORK PROBLEMS

- 9.1 For a separations process it is necessary to determine the VLE compositions of a mixture of ethyl bromide and *n*-heptane at 30°C. At this temperature the vapor pressure of pure ethyl bromide is 0.7569 bar, and the vapor pressure of pure *n*-heptane is 0.0773 bar. Calculate the bubble pressure and the composition of the vapor in equilibrium with a liquid containing 47.23 mol% ethyl bromide assuming ideal solution behavior. Compare the calculated pressure to the experimental value of 0.4537 bar.
- 9.2 Benzene and ethanol form azeotropic mixtures. Prepare a *y*-*x* and a *P*-*x*-*y* diagram for the benzene-ethanol system at 45°C assuming the mixture is ideal. Compare the results with the experimental data of Brown and Smith, *Austral. J. Chem.* 264 (1954). (*P* in bars)

x_e	0	0.0374	0.0972	0.2183	0.3141	0.4150	0.5199	0.5284	0.6155	0.7087	0.9591	1.000
y_e	0	0.1965	0.2895	0.3370	0.3625	0.3842	0.4065	0.4101	0.4343	0.4751	0.8201	1.000
<i>P</i>	0.2939	0.3613	0.3953	0.4088	0.4124	0.4128	0.41	0.4093	0.4028	0.3891	0.2711	0.2321

- 9.3 The following mixture of hydrocarbons is obtained as one stream in a petroleum refinery on a mole basis: 5% ethane, 10% propane, 40% *n*-butane, 45% isobutane. Assuming the shortcut *K*-ratio model: (a) compute the bubble point of the mixture at 5 bar; (b) compute the dew point of the mixture at 5 bar; (c) find the amounts and compositions of the vapor and liquid phases that would result if this mixture were to be isothermally flash vaporized at 30°C from a high pressure to 5 bar.
- 9.4 Consider a mixture of 50 mol% *n*-pentane and 50 mol% *n*-butane at 14 bar.
- What is the dew point temperature? What is the composition of the first drop of liquid?
 - At what temperature is the vapor completely condensed if the pressure is maintained at 14 bar? What is the composition of the last drop of vapor?

Sample Mixing Rules for the Virial Equation of State

The virial equation mixing rule is derived theoretically using statistical mechanics.¹ Since the second virial coefficient represents two-body interactions, the second virial coefficient of a mixture represents the summation of these interactions over the pairwise interactions in the mixture. In a binary mixture for example, there are three pairwise interactions in the mixture: 1-1, 2-2, and 1-2 interactions.

$$B = \sum_i \sum_j y_i y_j B_{ij} \quad 10.1$$

which for a binary mixture becomes

$$B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad 10.2$$

where the pure component virial coefficients are indicated by identical subscripts on the virial coefficients. In other words, B_{11} represents the contribution of 1-1 interactions, B_{22} represents 2-2 interactions, B_{12} represents the contribution of 1-2 interactions, and the mixing rule provides the mathematical method to sum up the contributions of the interactions. B_{12} is called the *cross coefficient*, indicating that it represents two-body interactions of unlike molecules. In the above sum, it is understood that B_{12} is equivalent to B_{21} . *The cross coefficient B_{12} is not the virial coefficient for the mixture.*

! *Combining rules* are used to quantify the parameters that represent unlike molecule interactions.

To obtain the cross coefficient, B_{12} , we must create a *combining rule* to propose how the cross coefficient depends on the properties of the pure components 1 and 2. For the virial coefficient, the relationship between the pair potential and the virial coefficient was given in Chapter 6. However, this level of rigor is rarely used in engineering applications. Rather, *combining rules* are created to use the corresponding state correlations developed for pure components in terms of T_{c12} and P_{c12} . The combining rules used to determine the values of the cross coefficient critical properties are:

$$T_{c12} = (T_{c1} T_{c2})^{1/2} (1 - k'_{12}) \quad 10.3$$

! Binary interaction parameters are used to adjust the combining rule to better fit experimental data, if available.

The parameter k'_{12} is an adjustable parameter (called the binary interaction parameter) to force the combining rules to more accurately represent the cross coefficients found by experiment.² However, in the absence of experimental data, it is customary to set $k'_{12} = 0$.

$$V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2} \right)^3 \quad 10.4$$

$$Z_{c12} = \frac{1}{2} (Z_{c1} + Z_{c2}) \quad 10.5$$

and

$$\omega_{12} = \frac{1}{2} (\omega_1 + \omega_2) \quad 10.6$$

1. The derivation is too detailed to present here; however in Section 10.1, we offer a rationale for the form of Eqn. 10.1

2. Reid, R, Prausnitz, J.M., Poling, B. *The Properties of Gases and Liquids*, page 133, McGraw-Hill (1987).

$$U^E = \frac{x_1 x_2 a_{11} \frac{V_2}{V_1} + x_1 x_2 a_{22} \frac{V_1}{V_2} - 2x_1 x_2 a_{12} \frac{V_2 V_1}{V_1 V_2}}{x_1 V_1 + x_2 V_2} \quad 11.26$$

$$= \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} \left(\frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2 \frac{a_{12}}{V_1 V_2} \right)$$

The van Laar Equation

We can simplify the equation for the excess internal energy by arbitrarily defining a single symbol, “ Q ,” to represent the final term in the equation:

$$U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} Q \quad \text{where } Q \equiv \left(\frac{\sqrt{a_{11}}}{V_1} - \frac{\sqrt{a_{22}}}{V_2} \right)^2 \quad 11.26a$$

It would appear that this equation contains three unknown parameters (V_1 , V_2 , and Q), but van Laar recognized that it could be rearranged such that only two adjustable parameters need to be determined.

$$A_{12} = \frac{QV_1}{RT}; \quad A_{21} = \frac{QV_2}{RT}; \quad \frac{A_{12}}{A_{21}} = \frac{V_1}{V_2} \quad 11.26b$$

with the final result:

$$\frac{G^E}{RT} = \frac{U^E}{RT} = \frac{A_{12} A_{21} x_1 x_2}{(x_1 A_{12} + x_2 A_{21})} \quad 11.27$$

Differentiating using Eqn. 11.7 gives expressions for the activity coefficients,

$$\ln \gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12} x_1}{A_{21} x_2} \right]^2}; \quad \ln \gamma_2 = \frac{A_{21}}{\left[1 + \frac{A_{21} x_2}{A_{12} x_1} \right]^2} \quad 11.28 \quad \text{van Laar Model.}$$

Note: the parameter A_{12} and A_{21} for the van Laar and Margules equations have different values for the same data. Do not interchange them.

When applied to binary systems, it is useful to note that these equations can be rearranged to obtain A_{12} and A_{21} from γ_1 and γ_2 given any one VLE point. This is the simple manner of estimating the parameters that we will generally apply in this chapter. Methods of fitting the parameters in optimal fashion for many data are covered in Section 11.7.

$$A_{12} = (\ln \gamma_1) \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right]^2 \quad A_{21} = (\ln \gamma_2) \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right]^2 \quad 11.29$$

Extreme care must be used before accepting the values of Eqn. 11.29 applied to a single measurement because experimental errors can occasionally result in questionable parameter values. Eqns. 11.29 applied to the activity coefficients from Example 11.3 result in $A_{12} = 2.38$, $A_{21} = 1.15$ and G^E is plotted in Fig. 11.3.

approximate accessible compositions are shown. Since the design rule is that a single column cannot cross a separatrix, the practical boundary for distillate compositions from the feed F_1 is approximated by the region $F_1-D_1-D_2$. For a feed of composition F_2 , the practical region of attainable distillate compositions is approximated by the region $F_1-D_1-D_3$. Although an example with a maximum boiling azeotrope is not shown, systems with these azeotropes can be screened using the same lever rule techniques; however, the bottoms of the column will be affected by the azeotropes.

Heteroazeotropes—Systems with LLE

Ternary systems exhibiting LLE form minimum-boiling heteroazeotropes and can often be separated in a system of two columns as shown in Fig. 13.16. The LLE behavior often spans a separatrix on the residue curve map. This means that an overhead stream, D_M , can be condensed in a decanter, and one of the liquid phases will be on the same side of the separatrix as D_1 and can be returned into that column (left in the figure). The other decanter liquid phase will be on the other side of the separatrix and can be used as a feed to another column (right in the figure). An example of this procedure is given by the separation of ethanol + water using benzene. In this case, benzene is intentionally added to break the azeotrope and permit water to be recovered from one column and ethanol from the other column. The system involves an ethanol + benzene minimum boiling azeotrope, an ethanol + water minimum boiling azeotrope, and a benzene + water minimum boiling heteroazeotrope. The system has three separatrices. The ternary azeotrope, o , is the lowest boiling point in the system and it is the origin of the residue curves for all three regions. The left column operates in the right region of the residue curve map, and the right column operates in the upper left region. Care is taken to avoid having F_2 fall in the lower left region of the residue curve map; such a feed would result in a bottoms of benzene rather than ethanol. Illustrative material balance lines are provided on the diagram, and the LLE curve is superimposed on the residue curve map to clearly show how the tie lines span the separatrices. For this example, the residue curves, origin can be moved farther into the LLE region by increasing the system pressure.

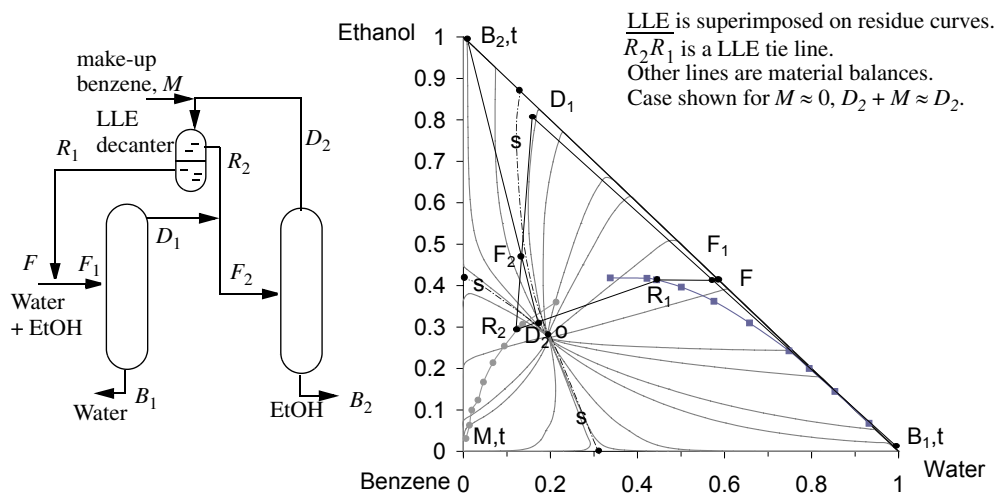


Figure 13.16 Illustration of the column configuration, residue curves and LLE behavior for the separation of ethanol and water using benzene, residue curves calculated using Aspen Plus[®] ver. 9.2 with UNIQUAC at 760 mmHg, LLE data at 25°C from Chang, Y.-I., Moultron, R.W., *Ind. Eng. Chem.*, 45(1953)2350. LLE tie lines are not plotted to avoid clutter, but tie-line data appear in pairs of points along the binodal line.

Suppose we make the approximation that ΔH_T^o is independent of temperature. That is, suppose $\Delta C_p = \Delta a = \Delta b = \Delta c = \Delta d = 0$. Then in the equations above, $J = \Delta H_R^o$ in Eqn. 14.29, or we can integrate Eqn. 14.24 directly to obtain what we refer to as the shortcut van't Hoff equation:

$$\ln\left(\frac{K_a}{K_{aR}}\right) = \frac{\Delta G_R^o}{RT_R} - \frac{\Delta G_T^o}{RT} = \frac{-\Delta H_R^o}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)$$

14.31  Shortcut van't Hoff equation.

This equation enables us to obtain rapid insight about the effects of temperature and we can often fill in the details later. It is such a popular equation that people often forget that it is only a shortcut, and not generally applicable to temperature ranges broader than about ± 100 K for high accuracy. As a particular observation, we take special note from the above equation that exothermic reactions ($\Delta H_T < 0$) lead to K_a decreasing as temperature increases, and endothermic reactions ($\Delta H_T > 0$) lead to K_a increasing as temperature increases. This means *equilibrium* conversion (for a specified feed) will increase with increasing temperature for endothermic reactions, and decrease with increasing temperature for exothermic reactions. This effect is illustrated in Fig. 14.1.

Example 14.6 Application of the shortcut van't Hoff equation

Apply the shortcut approximation to the vapor phase hydration of ethylene. This reaction has already been studied in the previous example, and the Gibbs energy of reaction and heat of reaction can be obtained from that example.

$$K_{a298} = \exp(+7546/8.314/298) = 21.03$$

$$\ln\left(\frac{K_a}{21.03}\right) = \frac{+45,625}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right)$$

$$K_a = 0.106 \text{ at } 145^\circ\text{C}; K_a = 0.0022 \text{ at } 320^\circ\text{C}$$

The results are very similar to the answer obtained by the general van't Hoff equation in Example 14.5.

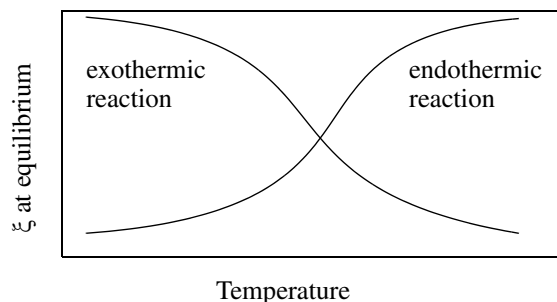
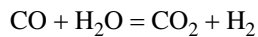
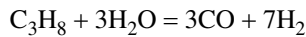


Figure 14.1 Qualitative behavior of equilibrium conversion for exothermic and endothermic reactions.

14.18 Hydrogen gas can be produced by the following reactions between propane and steam in the presence of a nickel catalyst:



Neglecting any other competing reactions:

- Compute the equilibrium constants at 700 K and 750 K.
- What is the equilibrium composition of the product gas if the inlet to the catalytic reactor is propane and steam in a 1:5 molar ratio at each of the temperatures and 1 bar?

14.19 Write and balance the chemical reaction of carbon monoxide forming solid carbon and carbon dioxide vapor. Determine the equilibrium constant at 700 and 750 K. Will solid carbon form at the conditions of problem 14.18?

14.20 Catalytic converters on automobiles are designed to minimize the NO and CO emissions derived from the engine exhaust. They generally operate between 400–600°C and 1 bar of pressure. K.C. Taylor (*Cat. Rev. Sci. Eng.*, 35:457, 1993) gives the following compositions (in ppm, molar basis) for typical exhaust from the engine:

NO	CO	O ₂	CO ₂	N ₂	H ₂	H ₂ O	hydrocarbons(~propane)
1050	6800	5100	135000	724000	2300	125000	750

The additional products of the effluent stream include NO₂, N₂O, N₂O₄, and NH₃. Estimate the compositions of all species at each temperature {400°C, 500°C, 600°C} and plot the ratio of NH₃/CO as a function of temperature. (Note: Use the options of the Solver software to set the precision of the results as high as possible.)

14.21 Styrene can be hydrogenated to ethyl benzene at moderate conditions in both the liquid and the gas phases. Calculate the equilibrium compositions in the vapor and liquid phases of hydrogen, styrene, and ethyl benzene at each of the following conditions:

- 3 bar pressure and 298 K, with a starting mole ratio of hydrogen to styrene of 2:1
- 3 bar pressure and 423 K, with a starting mole ratio of hydrogen to styrene of 2:1
- 3 bar pressure and 600 K, with a starting mole ratio of hydrogen to styrene of 2:1

14.22 Habenicht et al. (*Ind. Eng. Chem. Res.*, 34:3784, 1995) report on the reaction of t-butyl alcohol (TBA) and ethanol (EtOH) to form ethyltertiary-butyl ether (ETBE). The reaction is conducted at 170°C. A typical feed stream composition (in mole fraction) is:

TBA	EtOH	H ₂ O
0.027	0.832	0.141

Isobutene is the only significant by-product. Assuming that equilibrium is reached in the outlet stream, estimate the minimum pressure at which the reaction must be conducted in order to maintain everything in the liquid phase. Do isobutene or ETBE exceed their liquid solubility limits at the outlet conditions?

14.23 Limestone (CaCO₃) decomposes upon heating to yield quicklime (CaO) and carbon dioxide. At what temperature does limestone exert a decomposition pressure of 1 bar?

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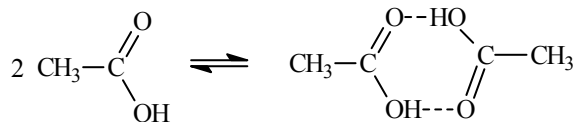
Table 15.1 *P-V-T evidence of association from the compressibility factors of saturated vapors.*

Acetic Acid			Benzene		
<i>T</i>	<i>P^{sat}</i> (mmHg)	<i>Z</i>	<i>T</i>	<i>P^{sat}</i> (mmHg)	<i>Z</i>
293	11.8	0.507	290	65.78	0.994
323	56.20	0.540	320	241.52	0.989
373	416.50	0.586	370	1240.60	0.962

In the case of acetic acid, the small compressibility factor is due to the dimerization of the carboxylic acid. Even though the pressure is very low, the compressibility factor approaches 0.5 because the number of molecules in the vapor is actually half the superficial amount, owing to the dimerization.¹ Note that the compressibility factor approaches unity as the temperature is increased. Why should the conversion to dimer be more complete at low temperature? Because association is an exothermic reaction and the van't Hoff relation clearly dictates that conversion of exothermic reactions decreases with increasing temperature. Another implication of associating fluids relative to non-associating fluids is that higher temperatures are needed to make the associating network break into a gas, and this means that T_c for an associating component will be significantly higher than a non-associating component of similar structure (e.g., H₂O vs. CH₄). The chemical association of acetic acid during dimerization is illustrated in Fig. 15.1. Note that the structure forms two hydrogen bonds simultaneously which makes the dimerization quite strong. Note also that a property of hydrogen bonding is that the O-H-O bond angle is nearly linear. This means that the carboxylic acid structure is close to a six-sided ring, not an eight-sided ring.

Dimerization of carboxylic acids is very common. In fact, the trend in LCEP discussed in Section 13 shows that dimerization is present even in long-chain fatty acids. Another commonly cited example of association is HF vapor, important in the manufacture of alternative refrigerants, which is modeled as (HF)_{*n*} with *n* predominately 6. Water and alcohols are extremely common substances in the chemical process industry and both exhibit association effects.

Hydrogen bonding is also common between different species. The hydrogen on a highly chlorinated molecule is easily hydrogen-bonded to a Lewis base, such as a carbonyl, ether, or amine group. Well-known examples are chloroform + acetone, chloroform + diethyl ether, and acetylene + acetone, as depicted in Fig. 15.2.

**Figure 15.1** *Schematic of association in acetic acid.*

1. The superficial number of moles is given by the species mass divided by the molecular weight of the monomer. On a superficial basis, we ignore the effect of association to dimers, trimers, etc.

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where for the monomers, $K_{a,i} = 1$. Once the $K_{a,i}$ are known, then x_{AM} and x_{BM} can be determined by solving these two equations. Subsequently, all other x_i and γ_A, γ_B can be calculated. If γ_A, γ_B are known from experiment, and the complex stoichiometry is known, $K_{a,i}$ values can be adjusted to fit the data using optimization methods. FORTRAN code is provided for solving for the true species for given values of $K_{a,i}$ in the program IChemT.exe.

 IChemT.exe

For ideal chemical theory applied to the vapor phase, the x_i are replaced with y_i and Eqn. 15.1 is expressed as $y_i = K_{a,i} P^{(a_i + b_i - 1)} \frac{a_i}{y_{AM}} \frac{b_i}{y_{BM}}$. Eqns. 15.18 and 15.20 then become

$$\sum_i K_{a,i} P^{(a_i + b_i - 1)} \frac{a_i}{y_{AM}} \frac{b_i}{y_{BM}} - 1 = 0 \quad (\text{ig}) 15.23$$

$$\sum_i (b_i y_A - a_i y_B) K_{a,i} P^{(a_i + b_i - 1)} \frac{a_i}{y_{AM}} \frac{b_i}{y_{BM}} = 0 \quad (\text{ig}) 15.24$$

These equations are marked as ideal gas equations since they are ideal gas equations from the perspective of the true solution. As with the liquid-phase calculation, if the $K_{a,i}$ values are known, y_{AM} and y_{BM} can be determined. The code IChemT.exe can also be used if values for $K_{a,i} P^{(a_i + b_i - 1)}$ are used when prompted for $K_{a,i}$.

Example 15.1 Compressibility factors in associating/solvating systems

Derive a formula to relate the true mole fractions to the compressibility factor of a vapor phase where the true species follow the ideal gas law.

Solution: A vessel of volume \underline{V} holds n_o superficial moles. However, experimentally, in the same total volume, there would be a smaller number of true moles n_T . Applying the ideal gas law,

$$P\underline{V} = n_T RT \quad \frac{P\underline{V}}{n_T RT} = 1 \quad (\text{ig}) 15.25$$

Experimentally, we wish to work in terms of the superficial number of moles,

$$Z = \frac{P\underline{V}}{n_o RT} = \frac{P\underline{V}}{n_T RT} \cdot \frac{n_T}{n_o} = \frac{n_T}{n_o} \quad (\text{ig})$$

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For chemical-physical theory applied to the vapor phase,

$$y_i = \frac{K_{a,i} P^{(a_i + b_i - 1)} (y_{AM} \hat{\phi}_{AM})^{a_i} (y_{BM} \hat{\phi}_{BM})^{b_i}}{\hat{\phi}_i} \quad \text{Eqns. 15.18 and 15.20 then become}$$

$$\sum_i \frac{K_{a,i} P^{(a_i + b_i - 1)} (y_{AM} \hat{\phi}_{AM})^{a_i} (y_{BM} \hat{\phi}_{BM})^{b_i}}{\hat{\phi}_i} - 1 = 0 \quad 15.29$$

$$\sum_i (b_i y_A - a_i y_B) \frac{K_{a,i} P^{(a_i + b_i - 1)} (y_{AM} \hat{\phi}_{AM})^{a_i} (y_{BM} \hat{\phi}_{BM})^{b_i}}{\hat{\phi}_i} = 0 \quad 15.30$$

The physical properties of the complex must also be modeled with this approach, and the same challenges for solving the equations are present as discussed above for chemical-physical theory of liquid phases.

An interesting study has been performed by Harris¹ for acetylene in *n*-hexane, butyrolactone, and *n*-methyl pyrrolidone at 25°C. In this study, a simplified van Laar model was used to model the physical deviations, which resulted in one physical parameter. Naturally, the acetylene + *n*-hexane does not exhibit solvation, but the other binaries do, with the pyrrolidone showing the strongest complexation. Further, the *n*-hexane system has positive deviations from Raoult's law across the composition range, the pyrrolidone shows negative deviations, and the lactone shows both positive and negative deviations. All three systems are accurately modeled using two parameters each—one chemical parameter and one physical parameter.

15.6 PURE SPECIES WITH LINEAR ASSOCIATION

Some species like water and alcohols form extended networks in solutions. The hydrogen bonding reactions usually occur so quickly that they can be assumed to be at equilibrium all the time.² It is desirable to investigate the implications of a more rigorous approach for pure species. Although the approach at first appears overwhelming, we always have just enough reaction constraints that the Gibbs phase rule works out the same for an associating component as for a single component.

We begin by describing the premise on which the model is based. We assume that association will occur by formation of linear chains of species. Dimers, trimers, tetramers, etc. will all form in a pure fluid, and the chains that form can be of infinite length. This does not require that long chains exist; the assumption simply does not forbid such behavior. Whether such behavior is found will be determined by the resulting model. Further, it should be recognized that the association that we describe is not static. The associations are truly reversible, and undergo frequent formation/decompositions; the equilibrium distributions simply tell us how many of a certain species will exist at a given instant. As one associated complex decomposes, another forms.

1. Harris, H. G., Prausnitz, J. M., *Ind. Eng. Chem. Fundam.*, 8:180 (1969).

2. An exception is the reaction of formaldehyde with water, c. Hasse and Maurer, *Fluid Phase Equilibria* 64:185 (1991).

602 Appendix B Mathematics

$$\int \frac{x^2 dx}{ax + b} = \frac{(ax + b)^2}{2a^3} - \frac{2b(ax + b)}{a^3} + \frac{b^2}{a^3} \ln(ax + b) \quad \text{B.15}$$

$$\int \frac{x^3 dx}{ax + b} = \frac{(ax + b)^3}{3a^4} - \frac{3b(ax + b)^2}{2a^4} + \frac{3b^2(ax + b)}{a^4} - \frac{b^3}{a^4} \ln(ax + b) \quad \text{B.16}$$

$$\int \frac{dx}{x(ax + b)} = \frac{1}{b} \ln\left(\frac{x}{ax + b}\right) \quad \text{B.17}$$

$$\int \frac{dx}{x^2(ax + b)} = -\frac{1}{bx} - \frac{a}{b^2} \ln\left(\frac{x}{ax + b}\right) \quad \text{B.18}$$

$$\int \frac{xdx}{(ax + b)^2} = \frac{b}{a^2(ax + b)} + \frac{1}{a^2} \ln(ax + b) \quad \text{B.19}$$

$$\int \frac{x^2 dx}{(ax + b)^2} = \frac{(ax + b)}{a^3} - \frac{b^2}{a^3(ax + b)} - \frac{2b}{a^3} \ln(ax + b) \quad \text{B.20}$$

$$\int \frac{x^3 dx}{(ax + b)^2} = \frac{(ax + b)^2}{2a^4} - \frac{3b(ax + b)}{a^4} + \frac{b^3}{a^4(ax + b)} + \frac{3b^2}{a^4} \ln(ax + b) \quad \text{B.21}$$

$$\int \frac{xdx}{(ax + b)^3} = \frac{-1}{a^2(ax + b)} + \frac{b}{2a^2(ax + b)^2} \quad \text{B.22}$$

$$\int \frac{x^2 dx}{(ax + b)^3} = \frac{2b}{a^3(ax + b)} - \frac{b^2}{2a^3(ax + b)^2} + \frac{1}{a^3} \ln(ax + b) \quad \text{B.23}$$

$$\int \frac{x^3 dx}{(ax + b)^3} = \frac{x}{a^3} - \frac{3b^2}{a^4(ax + b)} + \frac{b^3}{2a^4(ax + b)^2} - \frac{3b}{a^4} \ln(ax + b) \quad \text{B.24}$$

$$\int \frac{dx}{a + bx + cx^2} = \frac{1}{\sqrt{-q}} \ln \frac{(2cx + b - \sqrt{-q})}{(2cx + b + \sqrt{-q})} \quad \text{for } q < 0 \text{ where } q \equiv 4ac - b^2. \quad \text{B.25}$$

$$= \frac{2}{\sqrt{q}} \arctan \frac{2cx + b}{\sqrt{q}} \quad \text{for } q > 0$$

Integration by parts $\int u dv = uv - \int v du$

Numerical integration by trapezoidal rule:

$$\int_{x_0}^{x_n} f(x) dx = \Delta x \sum_{i=0}^n f(x_i) - \Delta x \left[\frac{f(x_0) + f(x_n)}{2} \right] \quad \text{B.26}$$

where Δx is a constant step size between discrete values of $f(x)$

See also Chapter 5 for additional mathematical relationships.