SEPARATION OPERATIONS 1 (0905451)

02 – CONCEPTS

ALI KH. AL-MATAR (aalmatar@ju.edu.jo)

Chemical Engineering Department, University of Jordan
Amman 11942, Jordan

Outline

- *K*-Values: Phase-Equilibrium Ratio/Distribution Coefficients
- Separation Factors
- Rigorous *K*-Value Formulations: VLE
  - Graphical Representation: Vapor Pressure
  - Graphical Representation: DePriester Charts at Low Temperature
  - Henry's Law
  - Enthalpy vs. Composition: Ponchon-Savarit Diagram
- Rigorous *K*-Value Formulations: LLE
- Rigorous *K*-Value Formulations: SVE
- Rigorous *K*-Value Formulations: SLE

K-Values: Phase-Equilibrium Ratio/Distribution Coefficients

- Vapor -Liquid Equilibria (VLE)
  - vapor–liquid equilibrium ratio

$$K_i = \frac{y_i}{x_i}$$

- Liquid-Liquid Equilibria (LLE)
  - partition coefficient, or liquid–liquid equilibrium ratio

$$K_{D_i} = \frac{x_i^{(1)}}{x_i^{(2)}}$$

Separation Factors

- Defined by forming ratios of distribution coefficients.
- Vapor -Liquid Equilibria (VLE)
  - Relative volatility $\alpha_{i,j}$

$$\alpha_{i,j} = \frac{K_i}{K_j}$$

- Liquid-Liquid Equilibria (LLE)
  - Relative selectivity $\beta_{i,j}$

$$\beta_{i,j} = \frac{K_{D_i}}{K_{D_j}}$$

- Separations are easy for very large values of $\alpha_{i,j}/\beta_{i,j}$.

Rigorous *K*-Value Formulations: VLE

- Equilibrium based on isofugacity condition:

$$\bar{f}_{i,V} = \bar{f}_{i,L}$$

  - Vapor fugacity given from an equation of state EOS (Phi) or simplification:

$$\bar{f}_{i,V} = \bar{\Phi}_{i,V} y_i P$$

  - Liquid fugacity given from an EOS (Phi), activity coefficients (Gamma) or simplification:

$$\bar{f}_{i,L} = \bar{\Phi}_{i,L} x_i P \quad \text{or} \quad \bar{f}_{i,L} = \gamma_{i,L} x_i f^{o}_{i,L}$$

- K-values:
  - Phi-Phi:

$$K_i = \frac{\bar{\Phi}_{i,L}}{\bar{\Phi}_{i,V}}$$

  - Gamma-Phi:

$$K_i = \frac{\gamma_{i,L} f^{o}_{i,L}}{\bar{\Phi}_{i,V} P} = \frac{\gamma_{i,L} \Phi_{i,L}}{\bar{\Phi}_{i,V}}$$

Rigorous *K*-Value Formulations: VLE

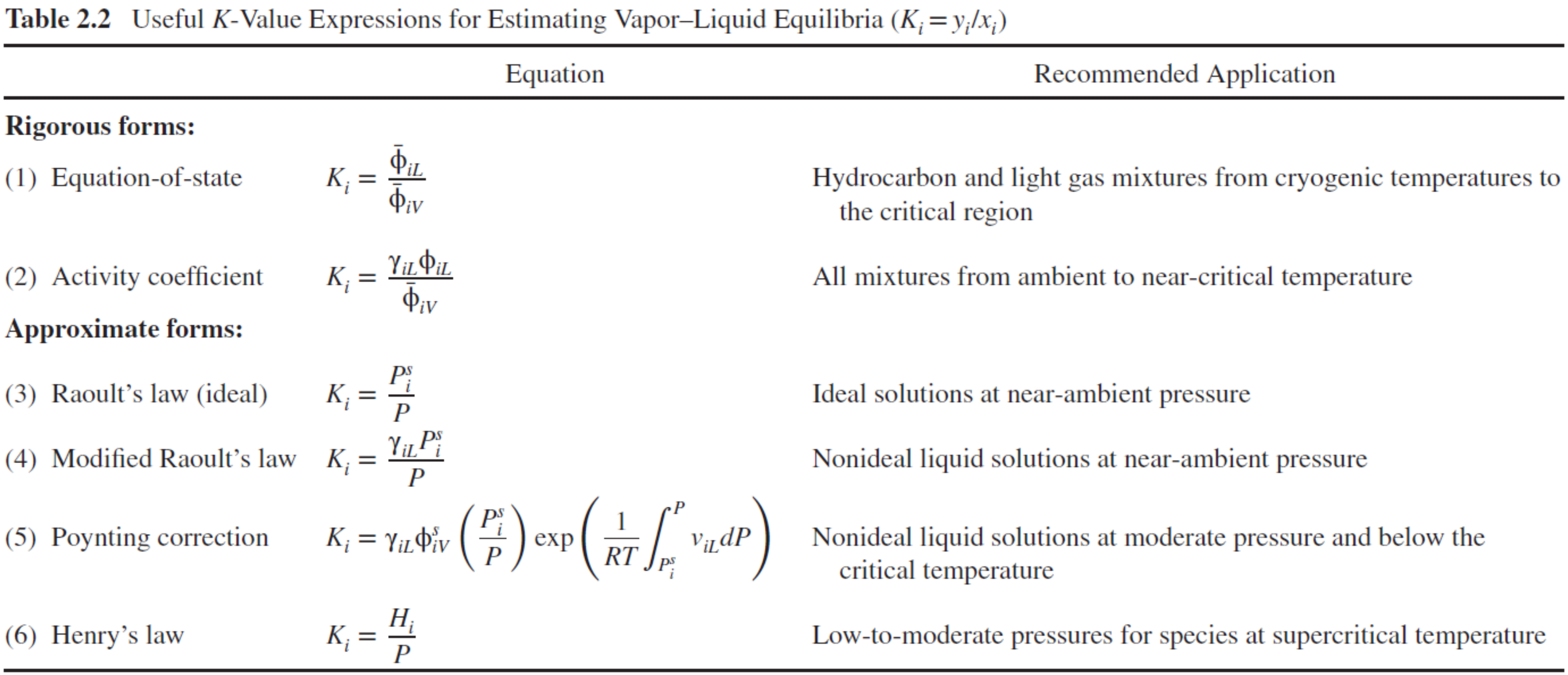


Table 2.2 Useful *K*-Value Expressions for Estimating Vapor–Liquid Equilibria ($K_i = y_i/x_i$)

	Equation	Recommended Application
Rigorous forms:		
(1) Equation-of-state	$K_i = \dfrac{\bar{\phi}_{iL}}{\bar{\phi}_{iV}}$	Hydrocarbon and light gas mixtures from cryogenic temperatures to the critical region
(2) Activity coefficient	$K_i = \dfrac{\gamma_{iL}\phi_{iL}}{\bar{\phi}_{iV}}$	All mixtures from ambient to near-critical temperature
Approximate forms:		
(3) Raoult's law (ideal)	$K_i = \dfrac{P_i^s}{P}$	Ideal solutions at near-ambient pressure
(4) Modified Raoult's law	$K_i = \dfrac{\gamma_{iL}P_i^s}{P}$	Nonideal liquid solutions at near-ambient pressure
(5) Poynting correction	$K_i = \gamma_{iL}\phi_{iV}^s\left(\dfrac{P_i^s}{P}\right)\exp\left(\dfrac{1}{RT}\displaystyle\int_{P_i^s}^{P} v_{iL}\,dP\right)$	Nonideal liquid solutions at moderate pressure and below the critical temperature
(6) Henry's law	$K_i = \dfrac{H_i}{P}$	Low-to-moderate pressures for species at supercritical temperature

Please read this presentation to grasp selecting a good thermodynamic model
https://www.researchgate.net/publication/283259774_Selecting_Fluid_Packages_Thermodynamic_Model_for_HYSYS_Aspen_Plus_ChemCAD_Process_Simulators

Graphical Representation: Vapor Pressure

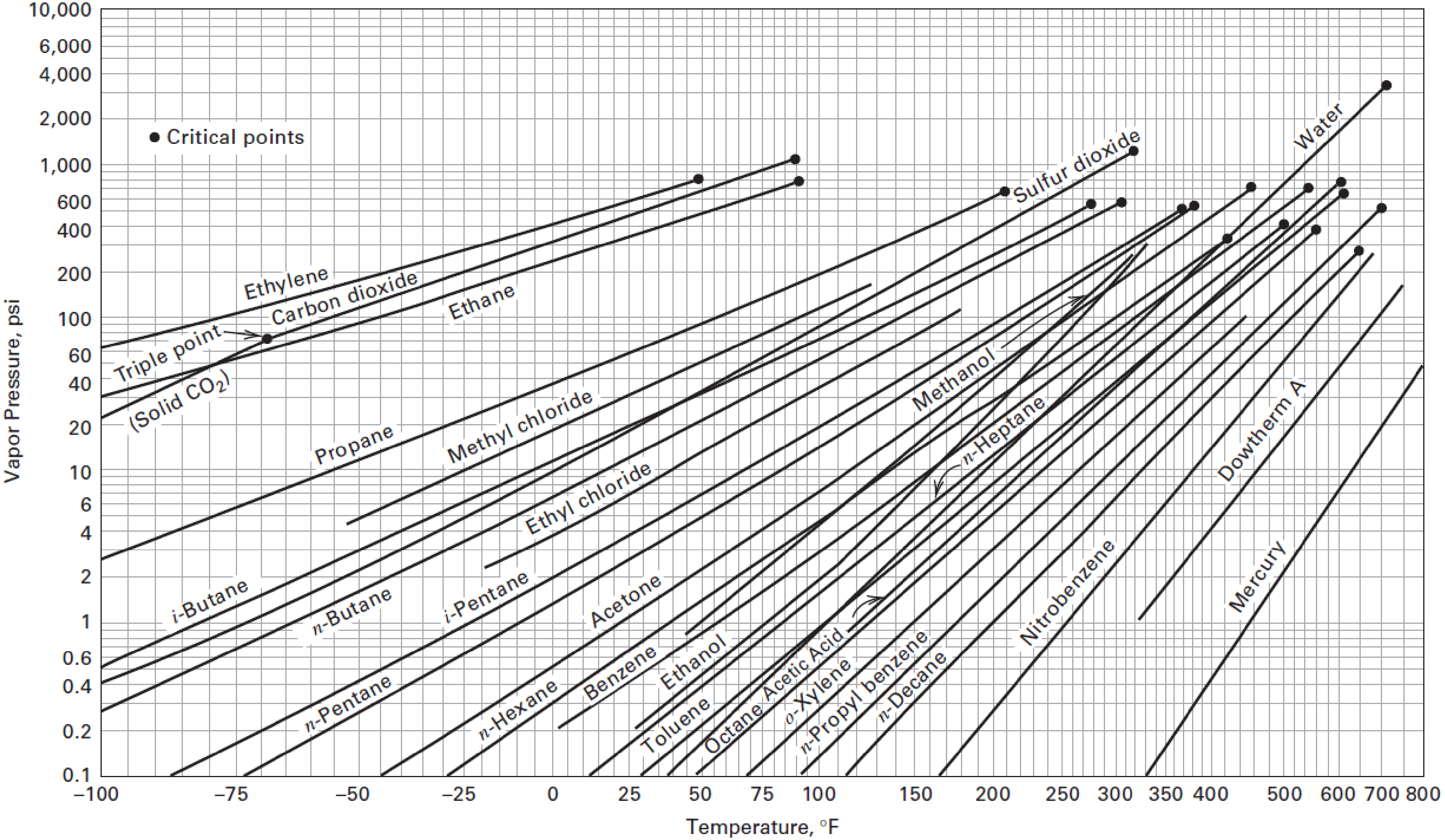
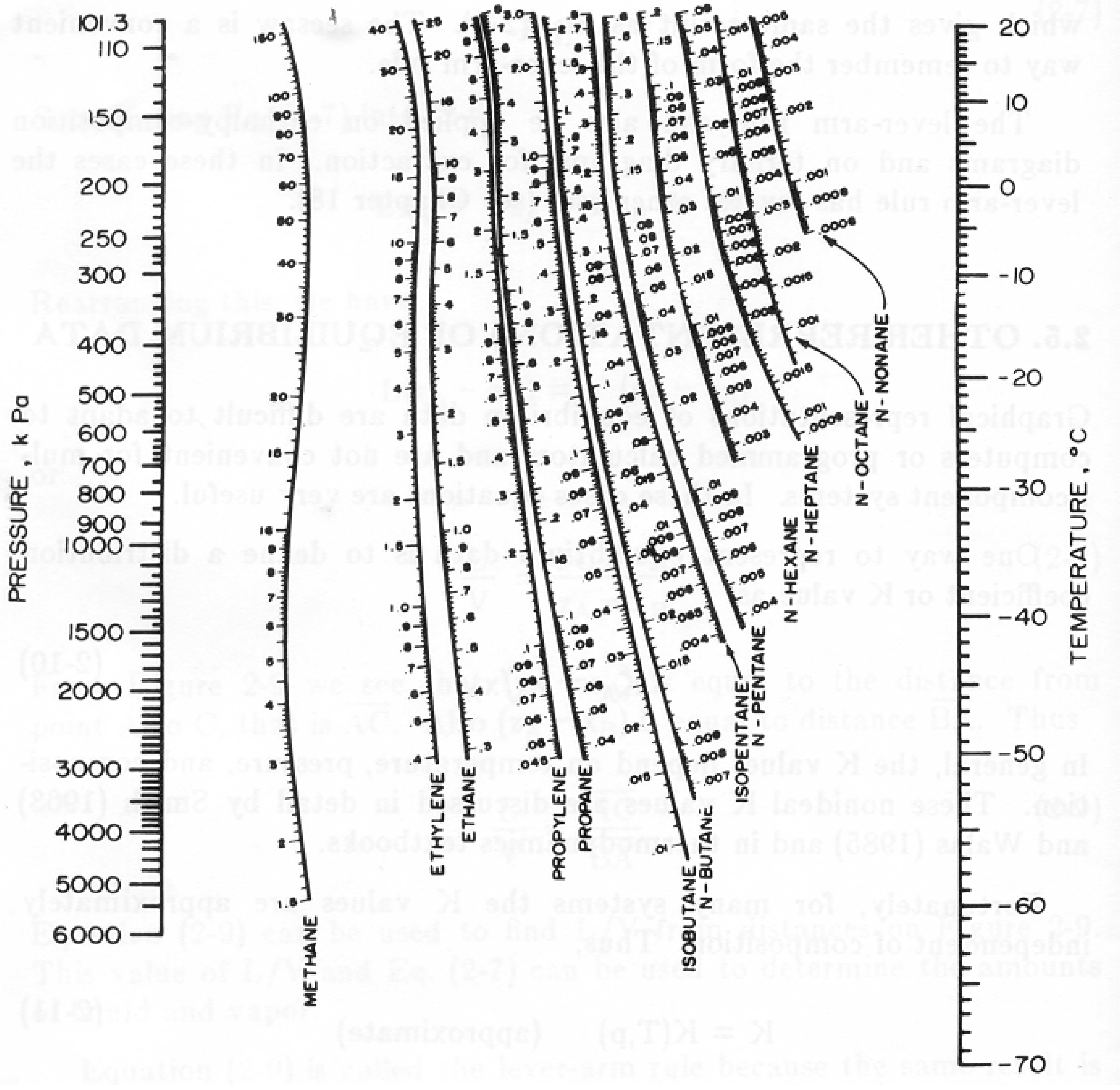


Figure 2.1 Vapor pressure of some common industrial chemicals.

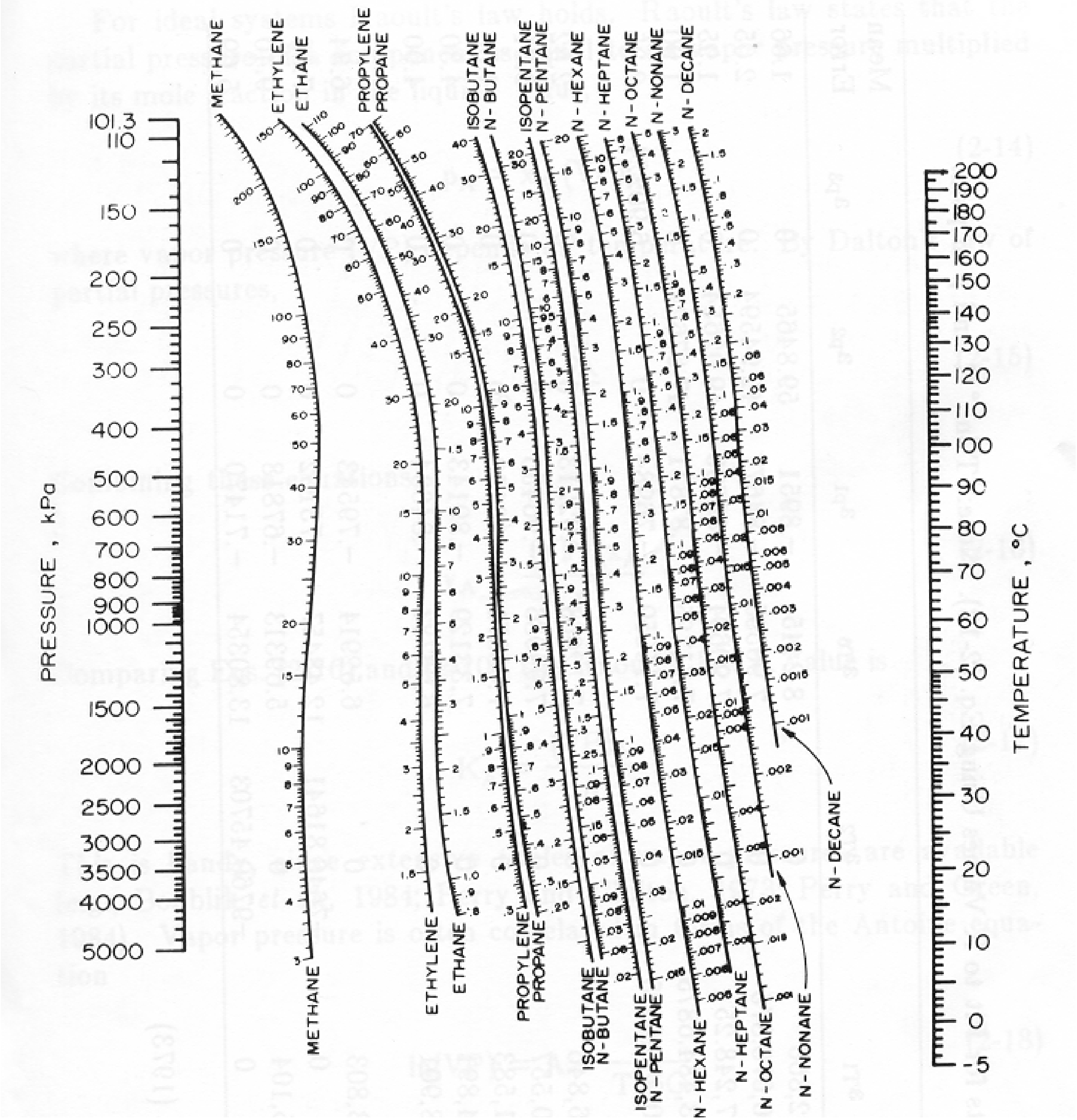
[Reproduced with permission from A.S. Faust, L.A. Wenzel, C.W. Clump, L. Maus, and L.B. Andersen, *Principles of Unit Operations*, John Wiley & Sons, New York (1960).]

Graphical Representation: DePriester Charts at Low Temperature



https://learncheme.com/simulations/thermodynamics/thermo-2/depriester-chart-for-hydrocarbons/

Graphical Representation: DePriester Charts at High Temperature



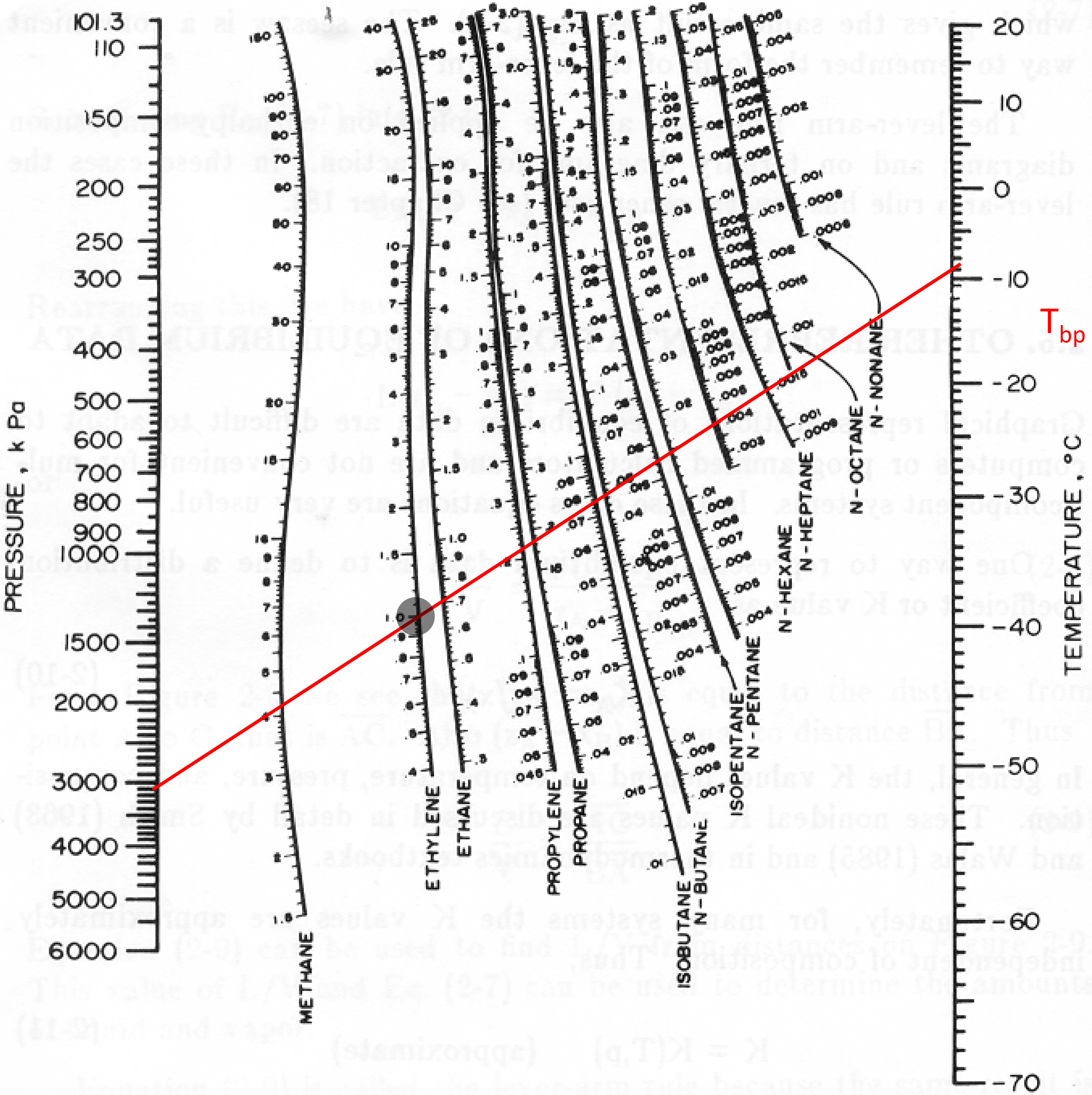
https://learncheme.com/simulations/thermodynamics/thermo-2/depriester-chart-for-hydrocarbons/

To determine the boiling point for a given component and pressure directly from the DePriester Charts set $K = 1.0$ for a pure component.

Example

Determine the boiling point temperature of ethylene at a pressure of $P = 3000$ kPa. Compare with the result obtained from Thermosolver software or any process simulator.

The lower the boiling point, the more volatile a component is.


PRESSURE, k Pa
101.3
110
150
200
250
300
400
500
600
700
800
900
1000
1500
2000
3000
4000
5000
6000
METHANE
ETHYLENE
ETHANE
PROPYLENE
PROPANE
ISOBUTANE
N-BUTANE
ISOPENTANE
N-PENTANE
N-HEXANE
N-HEPTANE
N-OCTANE
N-NONANE
TEMPERATURE, °C
20
10
0
-10
-20
-30
-40
-50
-60
-70

T_{bp} = - 9 °C

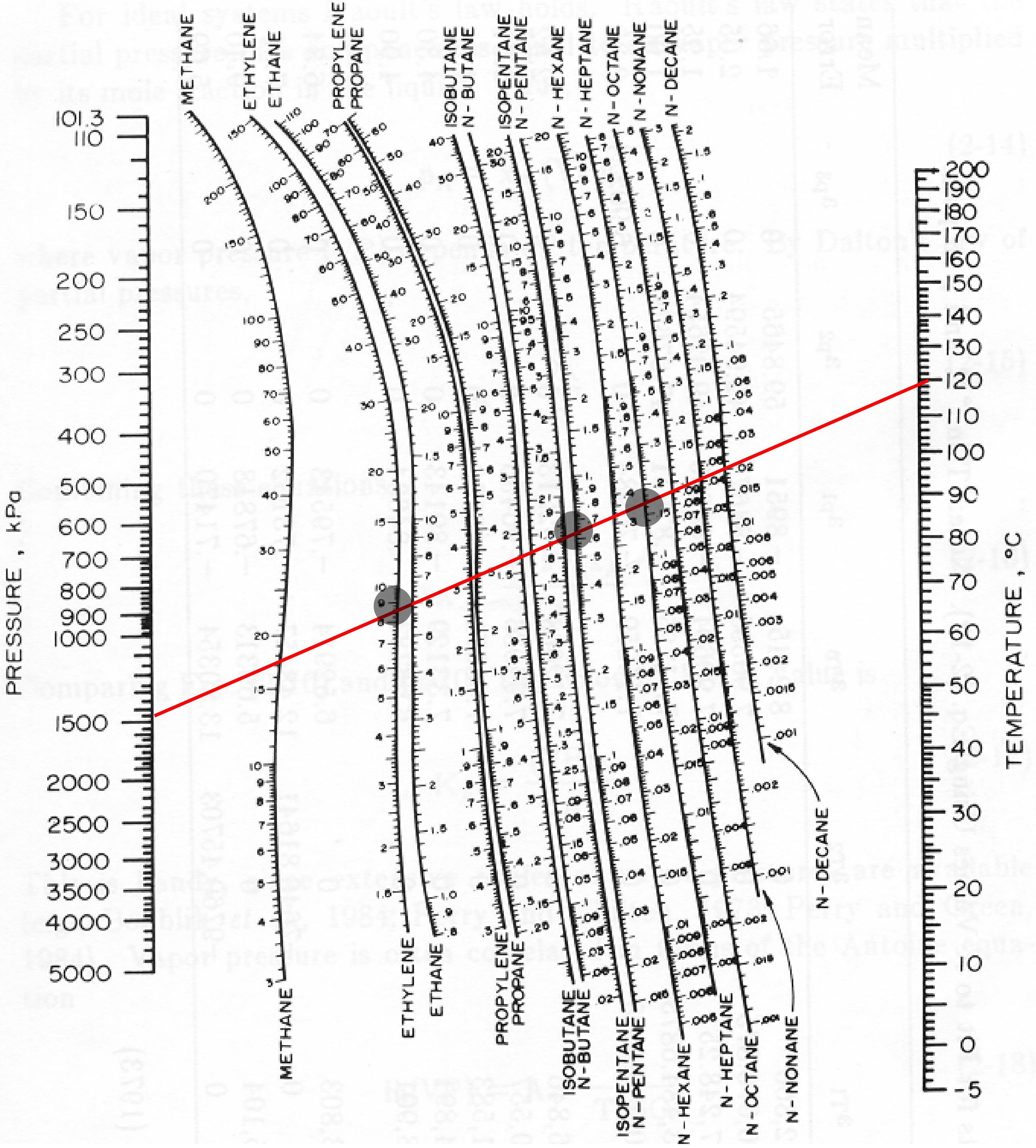
EXAMPLE

What are the equilibrium distribution coefficients, *K*, for a mixture containing: Ethylene, n-Pentane, and n-Heptane at $T = 120^oC$ and $P = 1500$ kPa?

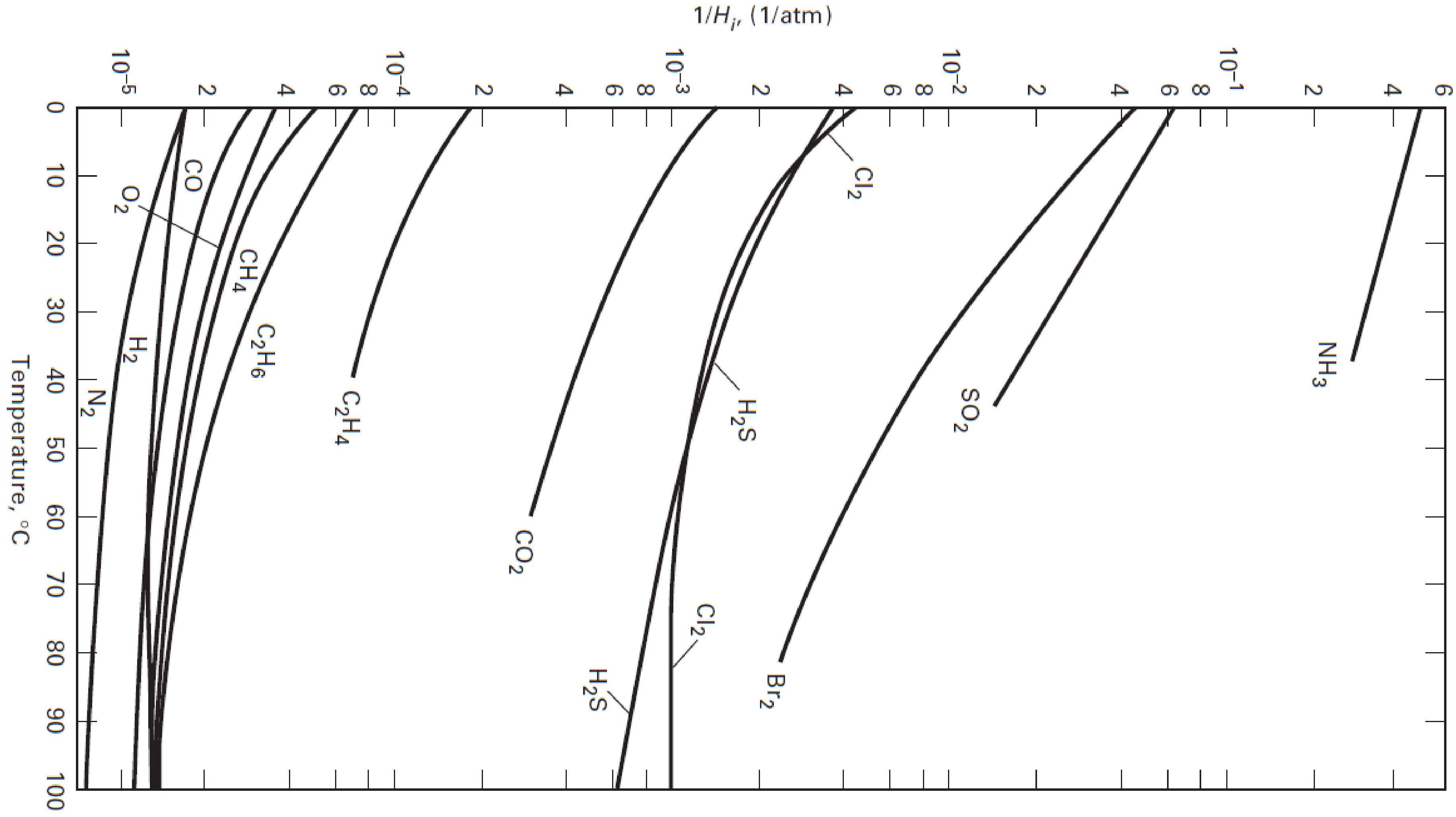
What can you say about the volatility of these compounds?

	K	T_{bp} (^oC)
Ethylene	8.5	-35.5
n-Pentane	0.64	153
n-Heptane	0.17	>200

Volatility trend: ethylene> n-pentane> n-heptane

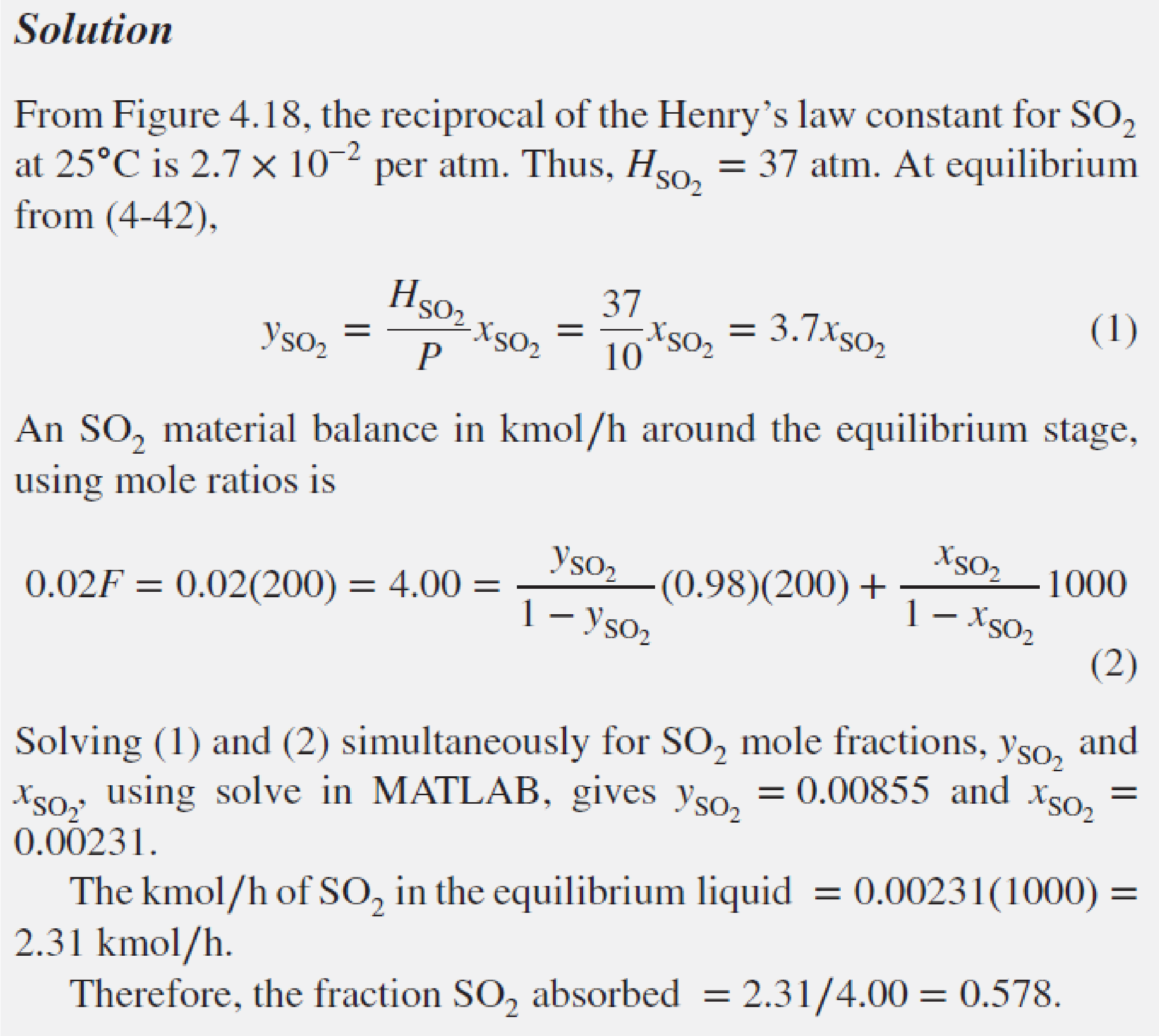

PRESSURE , kPa
101.3
110
150
200
250
300
400
500
600
700
800
900
1000
1500
2000
2500
3000
3500
4000
5000
METHANE
ETHYLENE
ETHANE
PROPYLENE
PROPANE
ISOBUTANE
N - BUTANE
ISOPENTANE
N - PENTANE
N - HEXANE
N - HEPTANE
N - OCTANE
N - NONANE
N - DECANE
TEMPERATURE , °C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-5

Henry’s Law Constant for Solubility of Gases in Water



EXAMPLE 4.10 Absorption of SO_2 with Water.

200 kmol/h of feed gas, *F*, containing 2 mol% SO_2 and 98 mol% air is contacted in a single equilibrium stage with 1,000 kmol/h of pure water, *W*, at 25°C and 10 atm to absorb SO_2. The total flow rates of equilibrium products are *G* and *L*. Determine the fraction of SO_2 absorbed. Neglect the absorption of air and the vaporization of water. Assume the applicability of Henry's law.



Solution

From Figure 4.18, the reciprocal of the Henry's law constant for SO_2 at 25°C is 2.7×10^{-2} per atm. Thus, $H_{SO_2} = 37$ atm. At equilibrium from (4-42),

$$y_{SO_2} = \frac{H_{SO_2}}{P} x_{SO_2} = \frac{37}{10} x_{SO_2} = 3.7 x_{SO_2} \qquad (1)$$

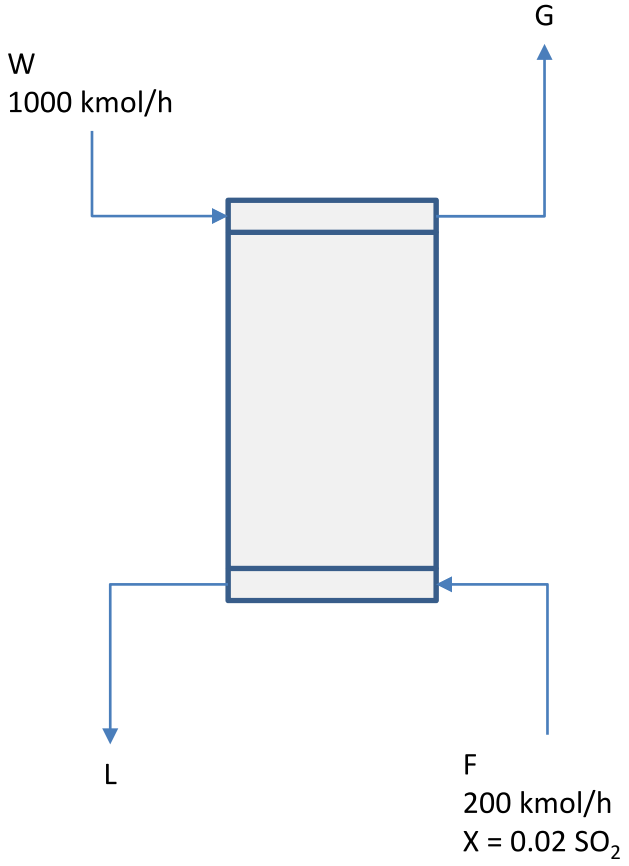
An SO_2 material balance in kmol/h around the equilibrium stage, using mole ratios is

$$0.02F = 0.02(200) = 4.00 = \frac{y_{SO_2}}{1 - y_{SO_2}}(0.98)(200) + \frac{x_{SO_2}}{1 - x_{SO_2}} 1000 \qquad (2)$$

Solving (1) and (2) simultaneously for SO_2 mole fractions, y_{SO_2} and x_{SO_2}, using solve in MATLAB, gives $y_{SO_2} = 0.00855$ and $x_{SO_2} = 0.00231$.

The kmol/h of SO_2 in the equilibrium liquid $= 0.00231(1000) = 2.31$ kmol/h.

Therefore, the fraction SO_2 absorbed $= 2.31/4.00 = 0.578$.



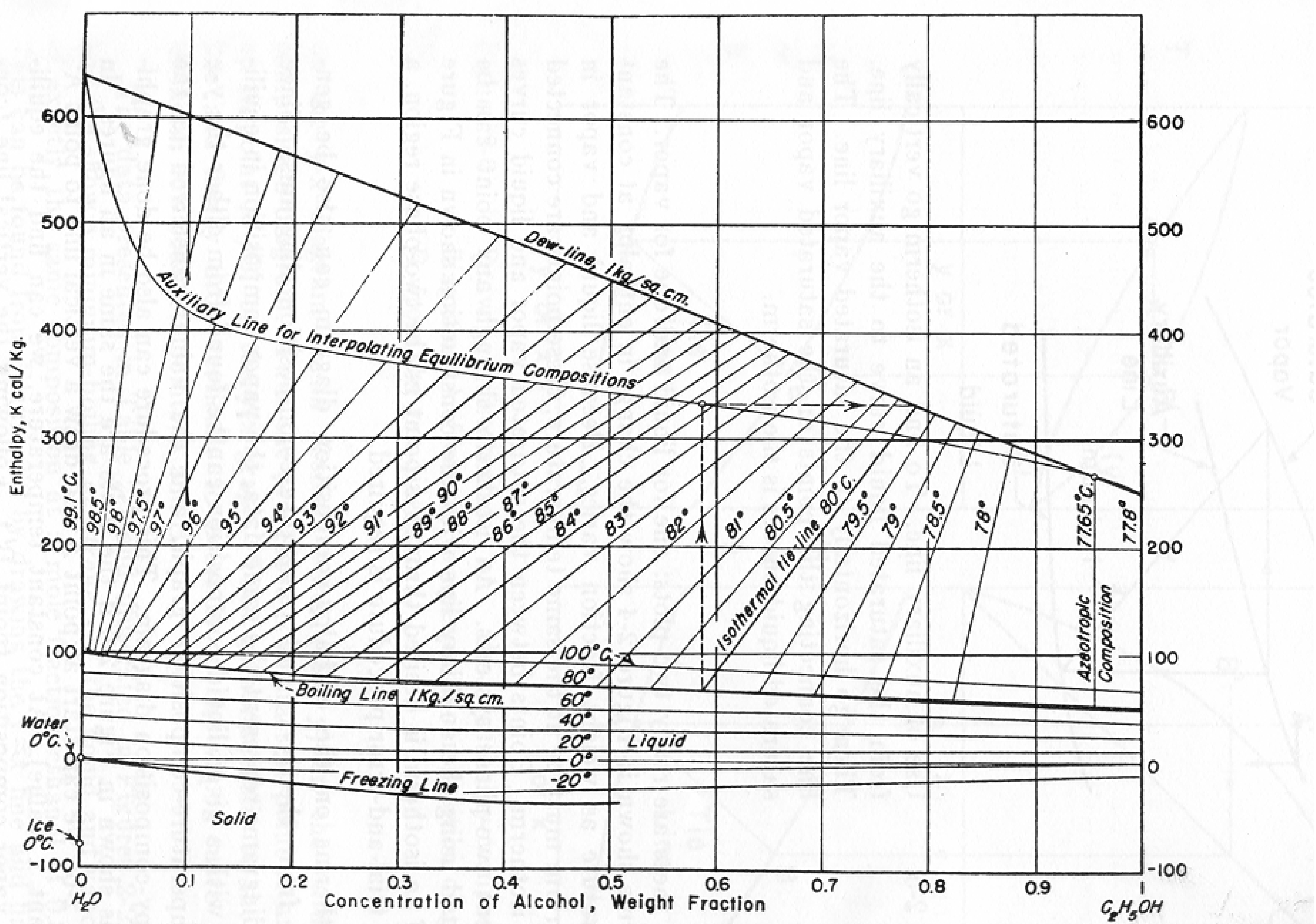
G

W
1000 kmol/h

L

F
200 kmol/h
X = 0.02 SO_2

Enthalpy vs. Composition: Ponchon-Savarit Diagram



Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2. (Bosnjakovic *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

Ponchon-Savarit Plots Remarks

- Plots 3 phases: solid, liquid, and vapor.
- Tie lines (isotherms) between the saturated liquid (boiling/bubble) curve and the saturated vapor (dew) curve.
- Any points between the bubble curve and the dew curve represent a two-phase; vapor-liquid system.
- An azeotrope formed is indicated by the composition at which the isotherm becomes vertical. Justify such a conclusion?
- Constant pressure of 1 kg/cm^2 (~0.97 atm).

Bubble and Dew Point Determination

- The bubble point temperatures and dew point temperatures can be determined from the enthalpy vs. composition diagram.
  - The compositions of the 1st bubble formed.
  - The composition of the last liquid drop.
- An auxiliary line is used to assist in these determination.

Converting Mole-Weight Fractions

- Enthalpy-composition plot is presented in terms of weight fractions.
  - For ethanol-water, conversion to mole fractions can be done using the molecular weights, $\mathrm{MW}_{\mathrm{EtOH}} = 46.07$ and $\mathrm{MW}_{\mathrm{w}} = 18.02$ g/mol.
- For a binary mixture:

$$x_1 = \frac{\dfrac{w_1}{\mathrm{MW}_1}}{\dfrac{w_1}{\mathrm{MW}_1} + \dfrac{w_2}{\mathrm{MW}_2}}$$

- For a multicomponent mixture of *C* components:

$$x_i = \frac{\dfrac{w_i}{\mathrm{MW}_\mathrm{i}}}{\displaystyle\sum_{j=1}^{C} \dfrac{w_j}{\mathrm{MW}_\mathrm{j}}}$$

EXAMPLE

Determine the bubble point temperature for a 40% alcohol solution with water at 1 kg/cm^2 using the *H*-*x* diagram.

T = 82.2°C

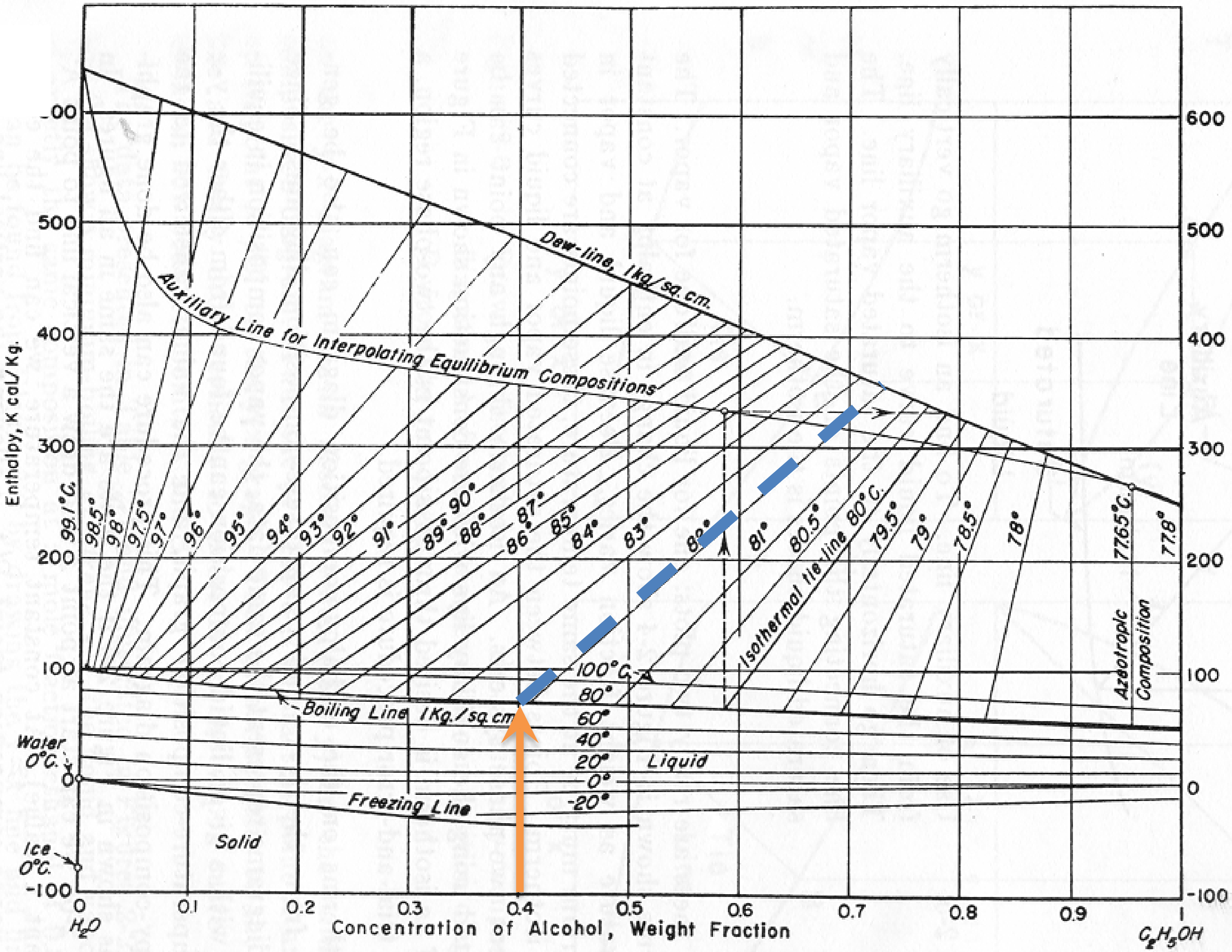


Figure 2-4. Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2. (Bosnjakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

EXAMPLE

Determine the composition of the first bubble for a 40% alcohol solution with water at 1 kg/cm^2 using the *H-x* diagram.

$y_1 \sim 0.73$

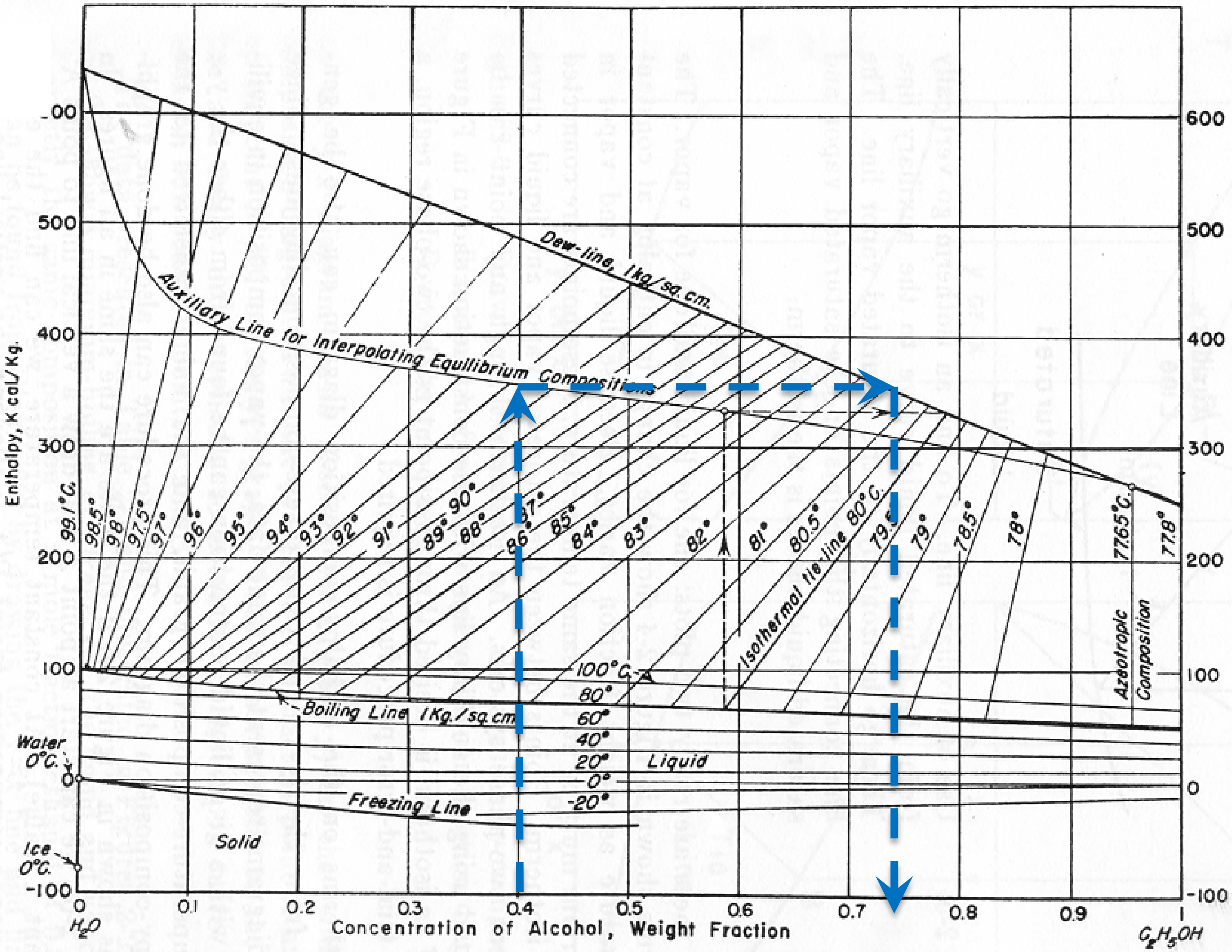


Figure 2-4. Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2. (Bosnjakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

EXAMPLE

Determine the dew point temperature for a 40% alcohol solution with water at 1 kg/cm^2 using the *H*-*x* diagram.

$T = 94.8^{o}C$

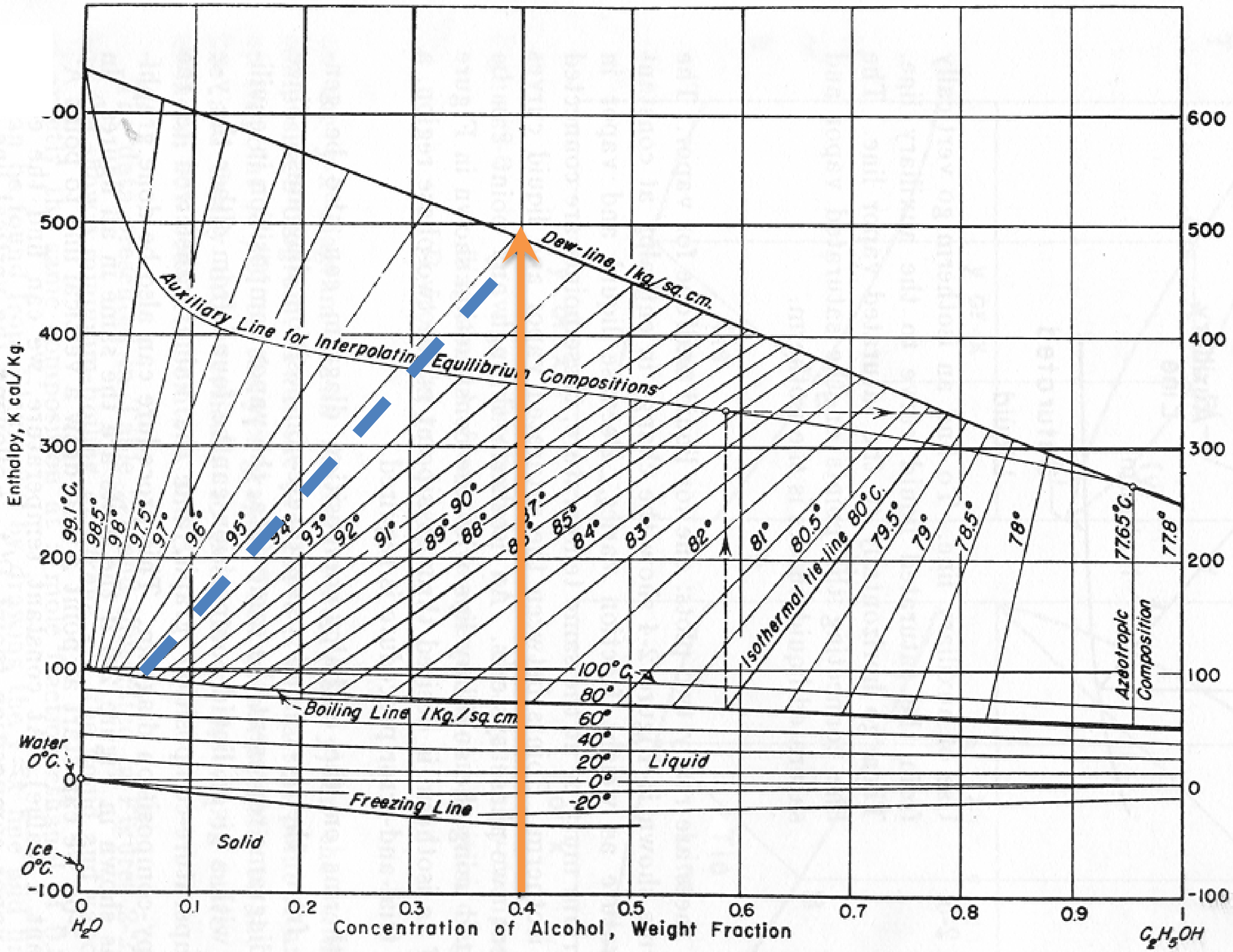


Figure 2-4. Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2. (Bosnjakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

EXAMPLE

Determine the composition at the dew point for a 40% alcohol solution with water at 1 kg/cm^2 using the *H*-*x* diagram.

$x_1 \sim 0.05$

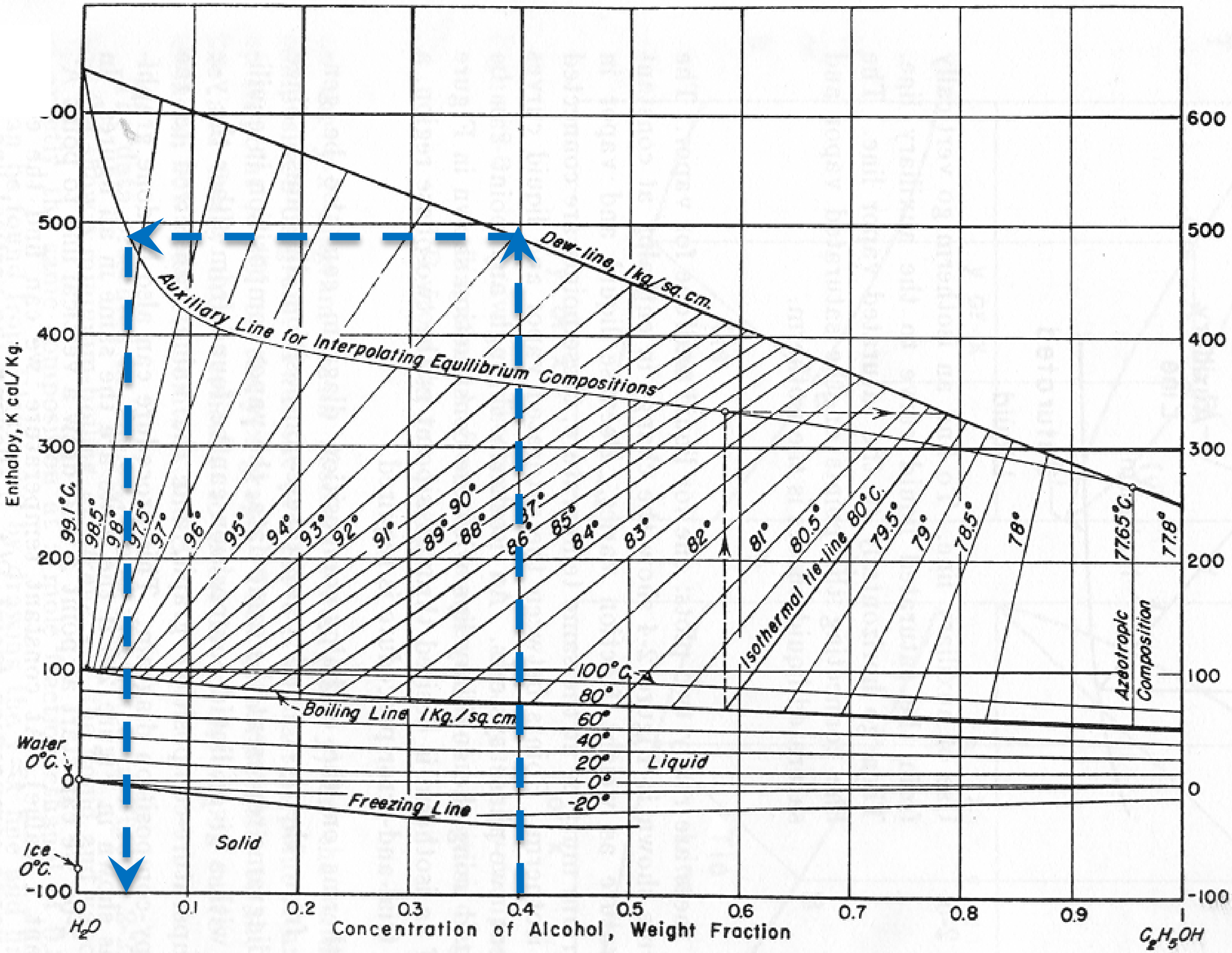
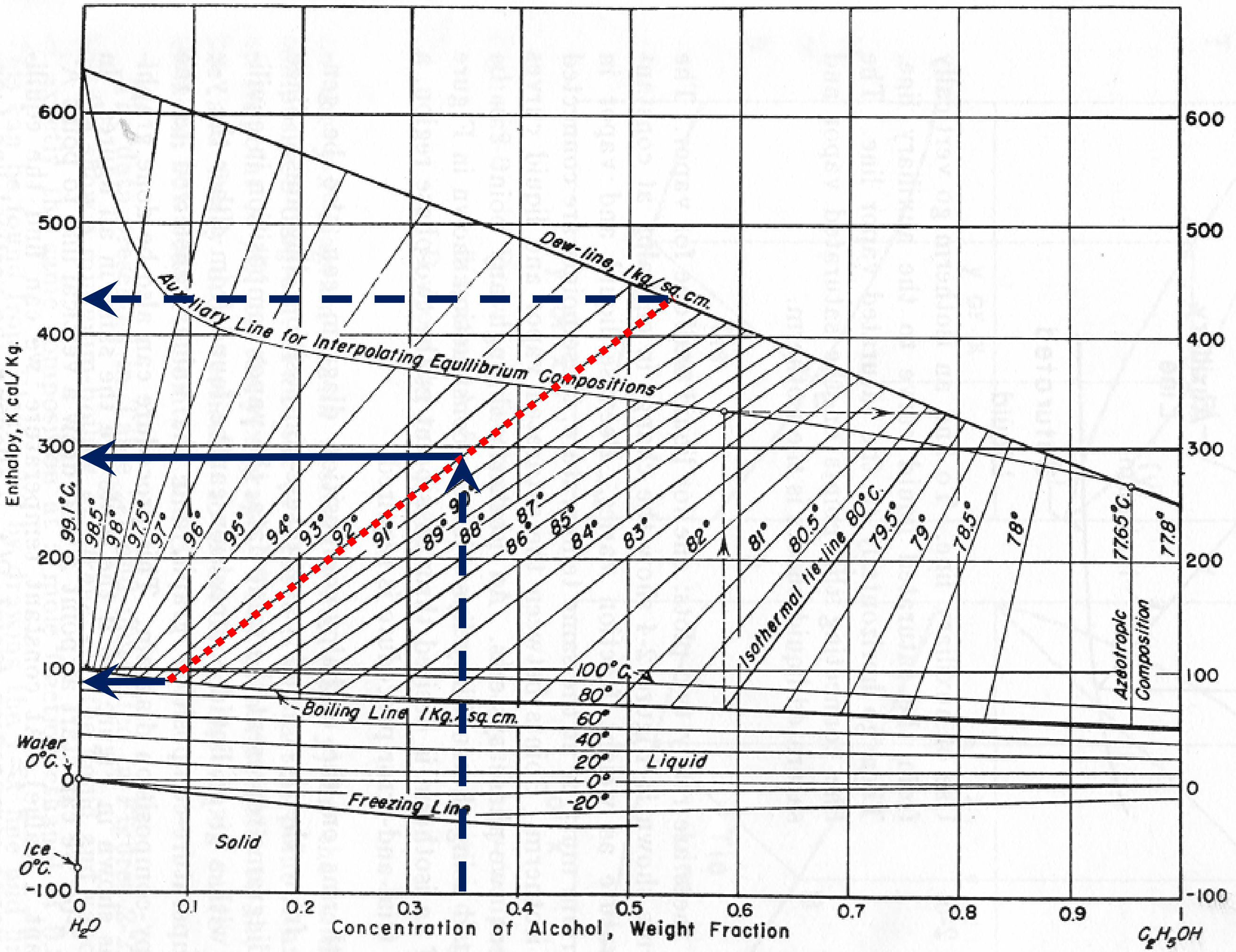


Figure 2-4. Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2. (Bosnjakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

Determining Enthalpy from Ponchon-Savarit Diagram

- The main reason of using Ponchon-Savarit diagram is to provide enthalpies of various streams.
  - These enthalpies are a cornerstone for carrying out energy balances.

- Example,
  - A feed mixture of 35% ethanol (weight %) at $T = 92^{o}$C and $P = 1$ kg/cm^2 and the mixture was allowed to separate into vapor and liquid, what would be the enthalpies of the feed, vapor, and liquid?



425

295

90

Figure 2-4. Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm^2. (Bosnjakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

Rigorous *K*-Value Formulations: LLE

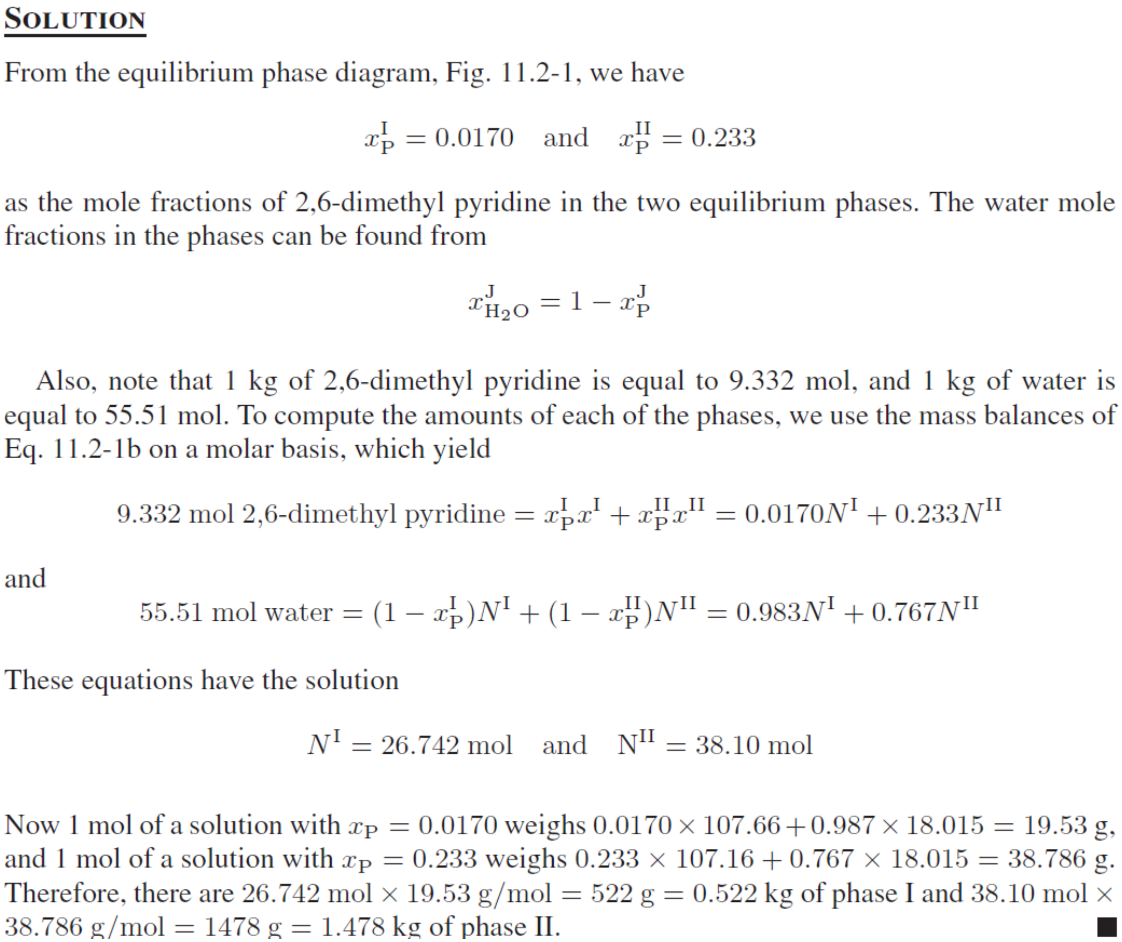
- Equilibrium based on isofugacity condition, superscripts (1) and (2) refer to the immiscible liquid phases:

$$\overline{f}_{i,L}^{(1)} = \overline{f}_{i,L}^{(2)}$$

- The rigorous formula for the distribution coefficient is given in terms of activity coefficients only:

$$K_{D_i} = \frac{x_i^{(1)}}{x_i^{(2)}} = \frac{\gamma_{i,L}^{(2)} f_{i,L}^{o,(2)}}{\gamma_{i,L}^{(1)} f_{i,L}^{o,(1)}} = \frac{\gamma_{i,L}^{(2)}}{\gamma_{i,L}^{(1)}}$$

EXAMPLE One kilogram of liquid 2,6-dimethyl pyridine (C_7H_9N, MW = 107.16) is mixed with 1 kg of water, and the mixture is heated to 80°C. Determine the compositions and total amounts of the two coexisting liquid phases.



SOLUTION

From the equilibrium phase diagram, Fig. 11.2-1, we have

$$x_{\mathrm{P}}^{\mathrm{I}} = 0.0170 \quad \text{and} \quad x_{\mathrm{P}}^{\mathrm{II}} = 0.233$$

as the mole fractions of 2,6-dimethyl pyridine in the two equilibrium phases. The water mole fractions in the phases can be found from

$$x_{\mathrm{H_2O}}^{\mathrm{J}} = 1 - x_{\mathrm{P}}^{\mathrm{J}}$$

Also, note that 1 kg of 2,6-dimethyl pyridine is equal to 9.332 mol, and 1 kg of water is equal to 55.51 mol. To compute the amounts of each of the phases, we use the mass balances of Eq. 11.2-1b on a molar basis, which yield

$$9.332 \text{ mol 2,6-dimethyl pyridine} = x_{\mathrm{P}}^{\mathrm{I}} x^{\mathrm{I}} + x_{\mathrm{P}}^{\mathrm{II}} x^{\mathrm{II}} = 0.0170N^{\mathrm{I}} + 0.233N^{\mathrm{II}}$$

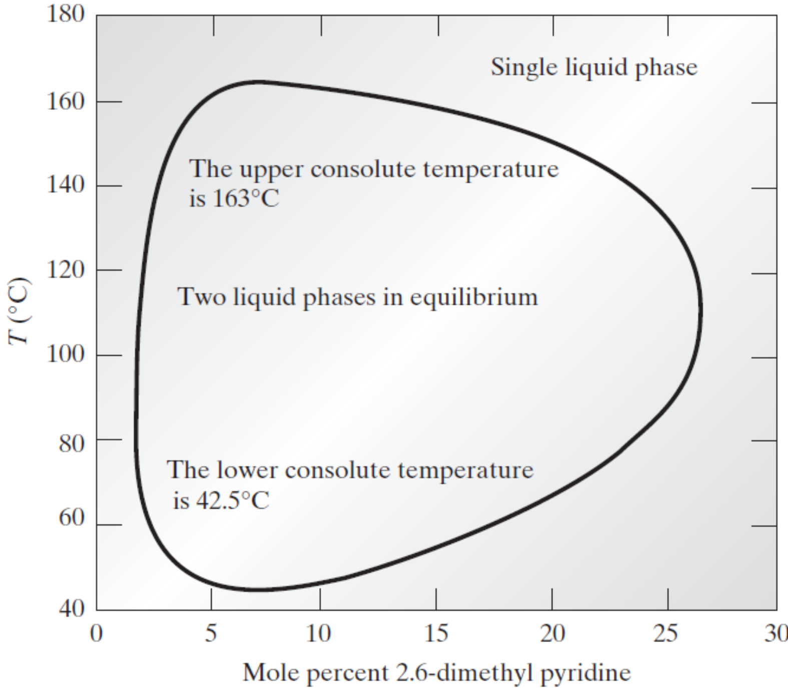
and

$$55.51 \text{ mol water} = (1 - x_{\mathrm{P}}^{\mathrm{I}})N^{\mathrm{I}} + (1 - x_{\mathrm{P}}^{\mathrm{II}})N^{\mathrm{II}} = 0.983N^{\mathrm{I}} + 0.767N^{\mathrm{II}}$$

These equations have the solution

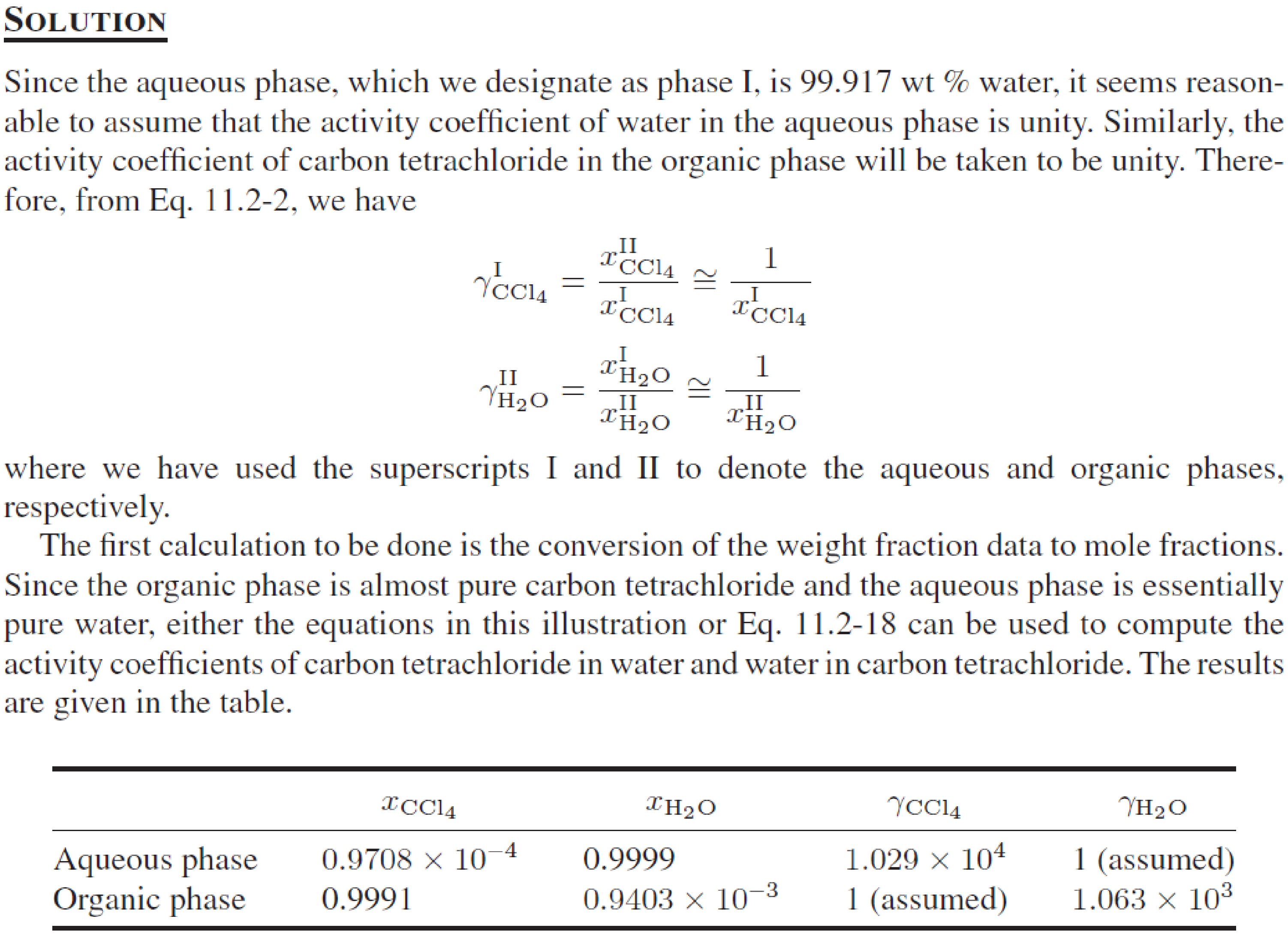
$$N^{\mathrm{I}} = 26.742 \text{ mol} \quad \text{and} \quad \mathrm{N}^{\mathrm{II}} = 38.10 \text{ mol}$$

Now 1 mol of a solution with $x_{\mathrm{P}} = 0.0170$ weighs $0.0170 \times 107.66 + 0.987 \times 18.015 = 19.53$ g, and 1 mol of a solution with $x_{\mathrm{P}} = 0.233$ weighs $0.233 \times 107.16 + 0.767 \times 18.015 = 38.786$ g. Therefore, there are 26.742 mol × 19.53 g/mol = 522 g = 0.522 kg of phase I and 38.10 mol × 38.786 g/mol = 1478 g = 1.478 kg of phase II. ■



The liquid-liquid phase diagram of 2,6-dimethyl pyridine and water, with composition in mole percent.

EXAMPLE From the data in Volume III of the *International Critical Tables* (McGraw-Hill, New York, 1929) we see that the equilibrium state in the carbon tetrachloride–water system at 25°C is two phases: one an aqueous phase containing 0.083 wt.% carbon tetrachloride, and the other an organic phase containing 0.011 wt. % water. Estimate the activity coefficient of CCl_4 in the aqueous phase and H_2O in the organic phase.



SOLUTION

Since the aqueous phase, which we designate as phase I, is 99.917 wt % water, it seems reasonable to assume that the activity coefficient of water in the aqueous phase is unity. Similarly, the activity coefficient of carbon tetrachloride in the organic phase will be taken to be unity. Therefore, from Eq. 11.2-2, we have

$$\gamma^{\mathrm{I}}_{\mathrm{CCl_4}} = \frac{x^{\mathrm{II}}_{\mathrm{CCl_4}}}{x^{\mathrm{I}}_{\mathrm{CCl_4}}} \cong \frac{1}{x^{\mathrm{I}}_{\mathrm{CCl_4}}}$$

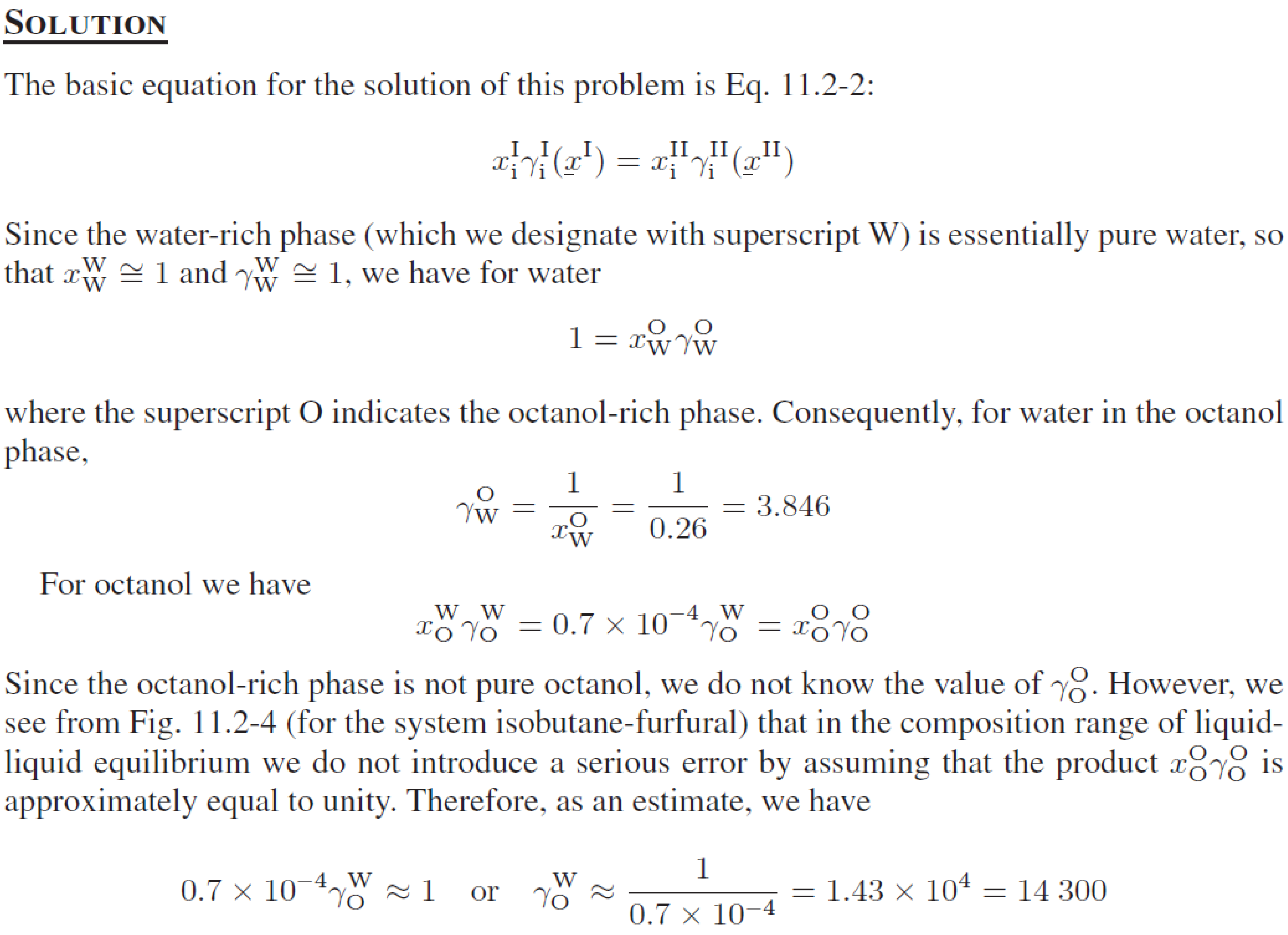
$$\gamma^{\mathrm{II}}_{\mathrm{H_2O}} = \frac{x^{\mathrm{I}}_{\mathrm{H_2O}}}{x^{\mathrm{II}}_{\mathrm{H_2O}}} \cong \frac{1}{x^{\mathrm{II}}_{\mathrm{H_2O}}}$$

where we have used the superscripts I and II to denote the aqueous and organic phases, respectively.

The first calculation to be done is the conversion of the weight fraction data to mole fractions. Since the organic phase is almost pure carbon tetrachloride and the aqueous phase is essentially pure water, either the equations in this illustration or Eq. 11.2-18 can be used to compute the activity coefficients of carbon tetrachloride in water and water in carbon tetrachloride. The results are given in the table.

	$x_{\mathrm{CCl_4}}$	$x_{\mathrm{H_2O}}$	$\gamma_{\mathrm{CCl_4}}$	$\gamma_{\mathrm{H_2O}}$
Aqueous phase	0.9708×10^{-4}	0.9999	1.029×10^{4}	1 (assumed)
Organic phase	0.9991	0.9403×10^{-3}	1 (assumed)	1.063×10^{3}

EXAMPLE When *n*-octanol and water are mixed, two liquid phases form. The water-rich phase is essentially pure water containing only 0.7x10-4 mole fraction *n*-octanol, while the n-octanol-rich phase contains approximately 0.26 mole fraction water. Estimate approximately the activity coefficient of *n*-octanol in water and water in *n*-octanol.



SOLUTION

The basic equation for the solution of this problem is Eq. 11.2-2:

$$x_{\mathrm{i}}^{\mathrm{I}}\gamma_{\mathrm{i}}^{\mathrm{I}}(\underline{x}^{\mathrm{I}}) = x_{\mathrm{i}}^{\mathrm{II}}\gamma_{\mathrm{i}}^{\mathrm{II}}(\underline{x}^{\mathrm{II}})$$

Since the water-rich phase (which we designate with superscript W) is essentially pure water, so that $x_{\mathrm{W}}^{\mathrm{W}} \cong 1$ and $\gamma_{\mathrm{W}}^{\mathrm{W}} \cong 1$, we have for water

$$1 = x_{\mathrm{W}}^{\mathrm{O}}\gamma_{\mathrm{W}}^{\mathrm{O}}$$

where the superscript O indicates the octanol-rich phase. Consequently, for water in the octanol phase,

$$\gamma_{\mathrm{W}}^{\mathrm{O}} = \frac{1}{x_{\mathrm{W}}^{\mathrm{O}}} = \frac{1}{0.26} = 3.846$$

For octanol we have

$$x_{\mathrm{O}}^{\mathrm{W}}\gamma_{\mathrm{O}}^{\mathrm{W}} = 0.7 \times 10^{-4}\gamma_{\mathrm{O}}^{\mathrm{W}} = x_{\mathrm{O}}^{\mathrm{O}}\gamma_{\mathrm{O}}^{\mathrm{O}}$$

Since the octanol-rich phase is not pure octanol, we do not know the value of $\gamma_{\mathrm{O}}^{\mathrm{O}}$. However, we see from Fig. 11.2-4 (for the system isobutane-furfural) that in the composition range of liquid-liquid equilibrium we do not introduce a serious error by assuming that the product $x_{\mathrm{O}}^{\mathrm{O}}\gamma_{\mathrm{O}}^{\mathrm{O}}$ is approximately equal to unity. Therefore, as an estimate, we have

$$0.7 \times 10^{-4}\gamma_{\mathrm{O}}^{\mathrm{W}} \approx 1 \quad \text{or} \quad \gamma_{\mathrm{O}}^{\mathrm{W}} \approx \frac{1}{0.7 \times 10^{-4}} = 1.43 \times 10^{4} = 14\,300$$

1. Since the concentration of *n*-octanol in water is so low, the value of essentially the value at infinite dilution.

2. The value of the infinite-dilution activity coefficient of *n*-octanol in water above is large, Consequently, although an activity coefficient represents a correction to ideal solution behavior, it can be a very large correction.

3. The value of the product $x_{O}^{o}\gamma_{O}^{o}$ cannot be greater than unity; otherwise a pure octanol phase would form. Therefore, the value of $x_{O}^{o}\gamma_{O}^{o}$ is likely to be somewhat less than unity, so our estimate above for the activity coefficient of octanol in water is too high, but probably only slightly so.

- The ***n*-octanol-water partition coefficient,** K_{ow} is a partition coefficient for the two-phase system consisting of *n*-octanol and water.
  - Frequently referred to by the symbol P.
  - Also called ***n*-octanol-water partition ratio.**
- Measure of the relationship between lipophilicity (fat solubility) and hydrophilicity (water solubility) of a substance.
  - Greater than one if a substance is more soluble in fat-like solvents such as n-octanol.
  - Less than one if it is more soluble in water.
- Values for log K_{ow} typically range between -3 (very hydrophilic) and +10 (extremely lipophilic/hydrophobic).

Selected log $P_{O/W}$ Values for Some Drugs/ Substances

Substance	log $P_{O/W}$	
Atorvastatin	4.00	Lower cholesterol and triglyceride (fats) levels in the blood (Lipitor)
Acetaminophen (paracetamol)	0.40	Pain reliever for mild to moderate pain, such as headaches, muscles aches, backache, and toothaches, and fevers (Panadol and Tylenol)
Naproxen	3.12	Reduce fever and relieve mild pain from headaches, muscle aches, arthritis, menstrual periods, the common cold, toothaches, and backaches
R-flurbiprofen	3.97	Relieve pain, tenderness, swelling, and stiffness caused by osteoarthritis and rheumatoid arthritis
Valsartan	3.37	Relaxes the blood vessels and lowers blood pressure.
Tramadol	2.64	Strong painkiller from a group of medicines called opiates, or narcotics. It's used to treat moderate to severe pain
Folic acid	0.10	Used for preventing and treating low blood levels of folate (folate deficiency) and high blood levels of homocysteine (hyperhomocysteinemia)
Omeprazole	2.23	Used to treat heartburn, stomach ulcers, reflux disease, or other conditions that cause too much stomach acid (Nexium)
Ciprofloxacin	-1.13	used to treat a number of bacterial infections, such as: uncomplicated urinary tract infections (UTIs) where other antibiotics are not suitable and complicated UTIs. chest infections (including pneumonia) skin and bone infections
Enalapril	-0.04	used to treat high blood pressure

S. Amézqueta, X. Subirats, E. Fuguet, M. Rosés, C. Ràfols, Chapter 6 Octanol-Water Partition Constant, Editor(s): Colin F. Poole, In Handbooks in Separation Science, Liquid-Phase Extraction, Elsevier, 2020, Pages 183-208,

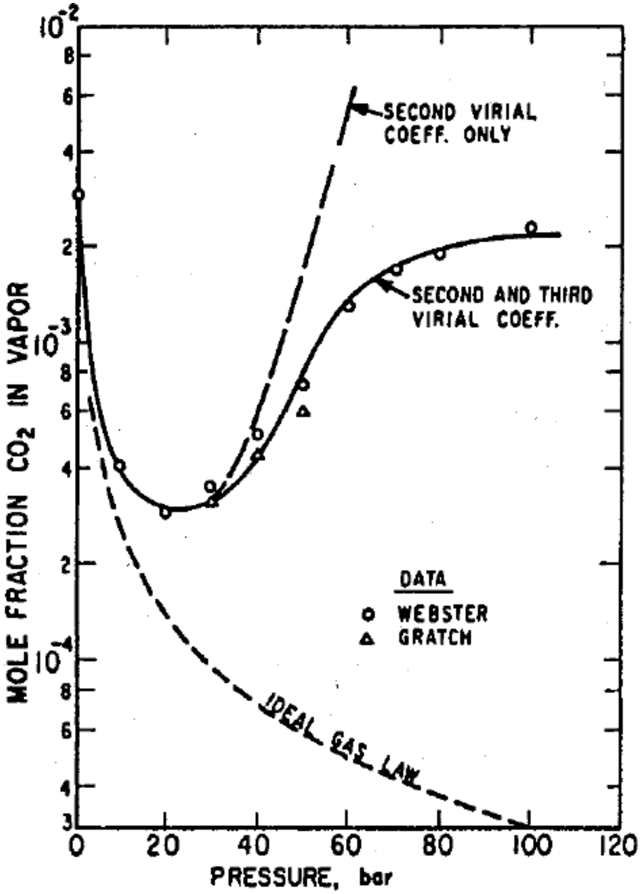
Rigorous *K*-Value Formulations: SVE

- For SVE, if the solid phase consists of just one of the components of the vapor phase:

$$\bar{f}_{i,S} = \bar{\Phi}_{i,V}\, y_i P$$

- At low pressures, fugacity coefficient approaches unity, and the fugacity of the solid is approximated by its vapor (sublimation) pressure

$$y_i = \frac{P_{i,S}^{\text{sub}}}{P}$$



Solubility of solid CO2 in air at 143 K.
From Prausnitz et al Fig. 5.38.

Rigorous *K*-Value Formulations: SLE

- For SLE, if the solid phase is a pure component:

$$f_{i,S} = \gamma_{i,L} x_i f_{i,L}^{o}$$

- At low pressure, the fugacity of a solid is approximated by vapor (sublimation) pressure to give, for a component in the solid phase:

$$x_i = \frac{P_{i,S}^{\text{sub}}}{\gamma_{i,L} P_{i,L}^{\text{vap}}}$$

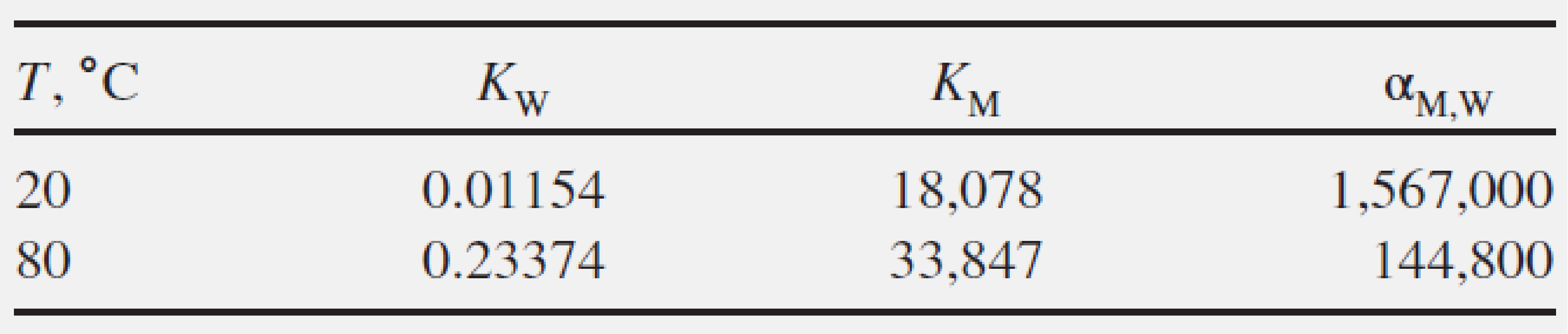
- Solid-liquid equilibria:
  - Crystallization
  - Selection of solvents for reaction mixtures
  - Plant safety assessment

EXAMPLE 2.1 *K*-Values from Raoult's and Henry's Laws

Estimate *K*-values and the relative volatility, $\alpha_{M,W}$, of a vapor–liquid mixture of water (W) and methane (M) at $P = 2$ atm, $T = 20$ and 80°C. What is the effect of *T* on the *K*-values?

Solution

At these conditions, water exists mainly in the liquid phase and will follow Raoult's law if little methane dissolves in the water. Because methane has a critical temperature of −82.5°C, well below the temperatures of interest, it will exist mainly in the vapor phase and follow Henry's law (2-31). The Aspen Plus process simulator is used to make the calculations using the Ideal Properties option with methane as a Henry's law component. The Henry's law constants for the solubility of methane in water are provided in the simulator data bank. The results are as follows:



T, °C	K_W	K_M	$\alpha_{M,W}$
20	0.01154	18,078	1,567,000
80	0.23374	33,847	144,800

For both temperatures, the mole fraction of methane in the water is less than 0.0001. The *K*-values for H_2O are low but increase rapidly with temperature. The *K*-values for methane are extremely high and change much less rapidly with temperature.

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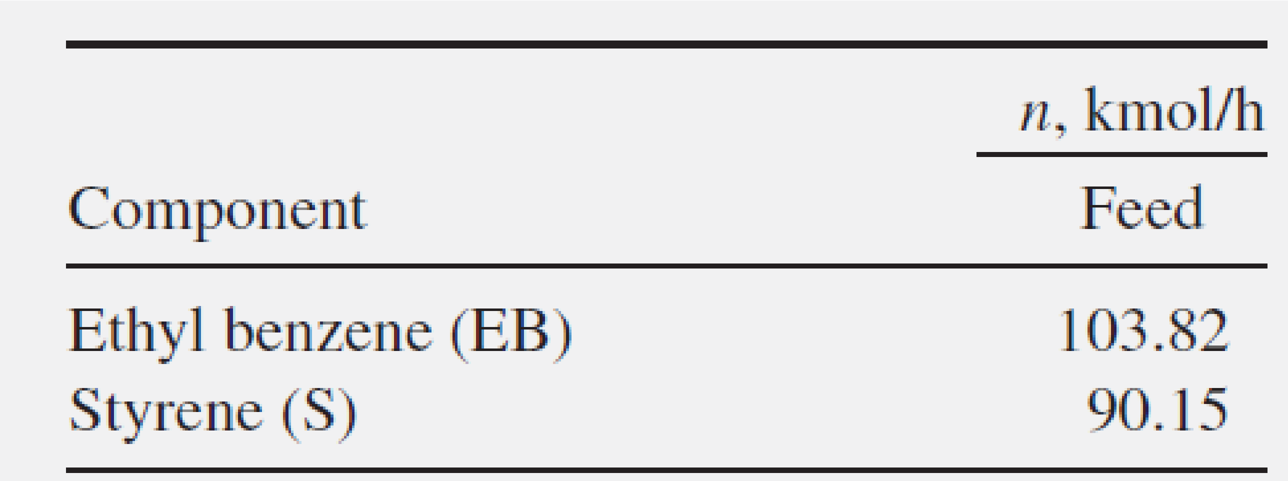
EXAMPLE 2.2 Thermodynamic Properties of an Ideal Mixture.

Styrene is manufactured by catalytic dehydrogenation of ethyl benzene, followed by vacuum distillation to separate styrene from unreacted ethyl benzene. Typical conditions for the feed are 77.9°C (351 K) and 100 torr (13.33 kPa), with the following flow rates:

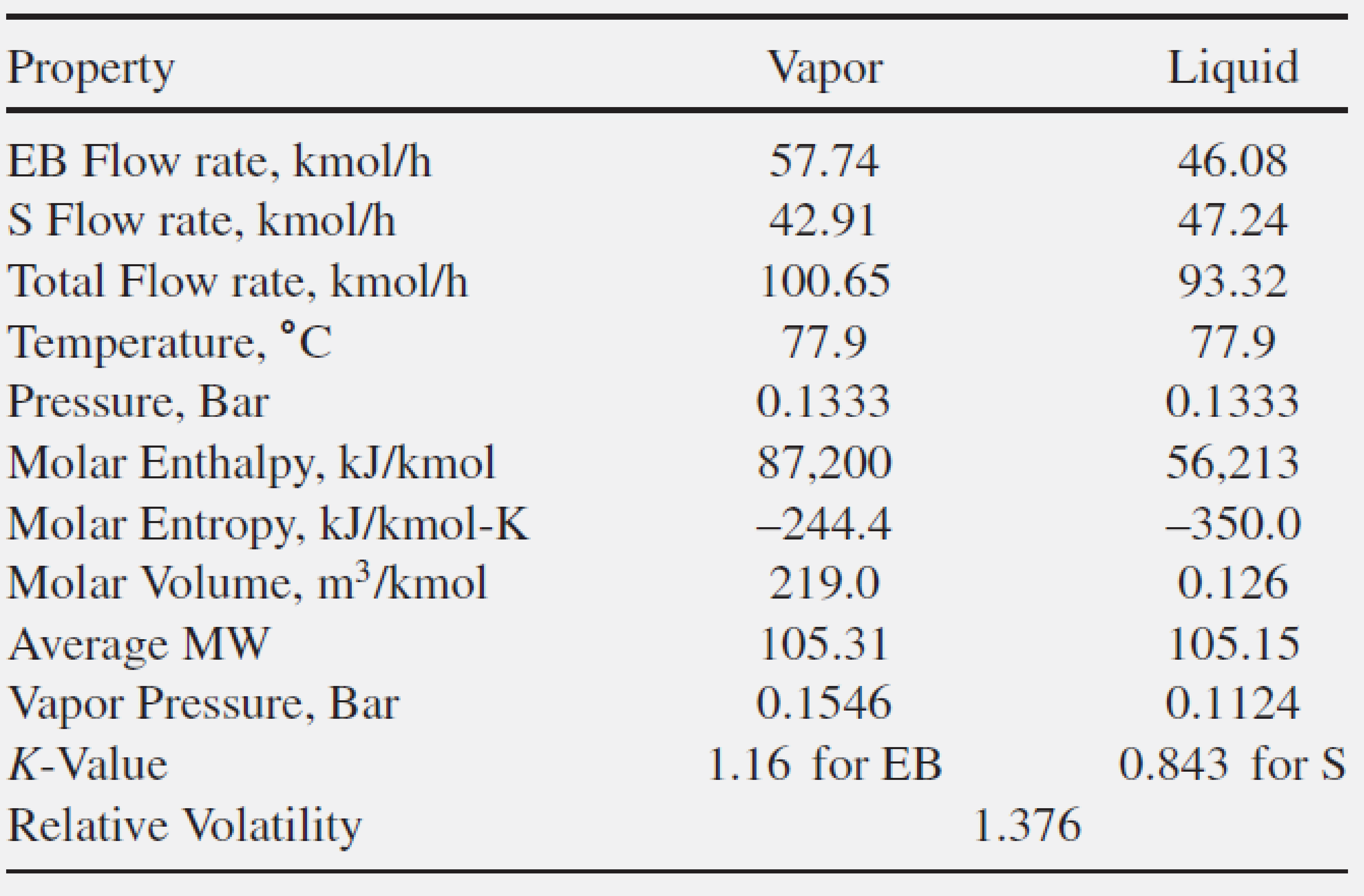


	n, kmol/h
Component	Feed
Ethyl benzene (EB)	103.82
Styrene (S)	90.15

Assuming that the ideal-gas law holds and that vapor and liquid phases exist and are ideal solutions, use a process simulator to determine the feed-stream phase conditions and the thermodynamic properties listed in Table 2.2. Also, compute the relative volatility, $\alpha_{EB,S}$.

Solution:

The Aspen Plus Simulator with the Ideal Properties option gives the following results where the datum is the elements (not the components) at 25°C and 1 atm.



Property	Vapor	Liquid
EB Flow rate, kmol/h	57.74	46.08
S Flow rate, kmol/h	42.91	47.24
Total Flow rate, kmol/h	100.65	93.32
Temperature, °C	77.9	77.9
Pressure, Bar	0.1333	0.1333
Molar Enthalpy, kJ/kmol	87,200	56,213
Molar Entropy, kJ/kmol-K	–244.4	–350.0
Molar Volume, m^3/kmol	219.0	0.126
Average MW	105.31	105.15
Vapor Pressure, Bar	0.1546	0.1124
K-Value	1.16 for EB	0.843 for S
Relative Volatility	1.376	

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Sources of Vapor-Liquid Equilibrium and Other Data

- Chemical Engineering and Materials Research Information Center, South Korea, https://www.cheric.org/research/kdb.
- Dortmund Data Bank (free VLE data), http://www.ddbst.com/ddb.html.
- NIST Chemistry Web Book, https://webbook.nist.gov.
- DIPPR database https://www.aiche.org/dippr.
- *Perry's Chemical Engineer's Handbook,* various editors: 3rd ed. (1950), 4th ed. (1963), 5th ed. (1973), 6th ed. (1984), 7th ed. (1997), 8th ed. (2008), and 9th ed. (2019), McGraw-Hill, New York.
- http://www.vle-calc.com/