Table 3.6 Enthalpy data for *n*-hexane/*n*-octane at 101 kPa. Enthalpy datum: $H_L = 0$ @ 0°F

	Enthalpy, Btu/lb			
	n-Hexane		*n*-Octane	
T, °F	H_L	H_V	H_L	H_V
100	55.5	210	57	203
125	70.5	220	65	214
150	85	230.5	80	225
175	100.5	241	95	237
200	117	253	109	248
225	133	266	125	260
250	150	278	140	272.5
275	167	290.5	157.5	285
300	185	303	173	298

Source. Data of J. B. Maxwell, *Data Book on Hydrocarbons*, D. Van Nostrand Co., New York, 1950, pp. 103, 105.

Table 3.7 Tabulated *H*-*y*, *H*-*x* data for *n*-hexane/*n*-octane at 101 kPa

	n-Hexane Mole Fractions		Mixture Enthalpy, Btu/lbmole	
T, °F	*x*	*y*	H_L	H_V
155.7	1.0	1.0	7,586	20,085
160	0.917	0.986	8,030	20,309
170	0.743	0.947	8,198	20,940
180	0.600	0.900	9,794	21,642
190	0.481	0.842	10,665	22,433
200	0.377	0.773	11,557	23,287
210	0.295	0.693	12,413	24,286
220	0.215	0.592	13,309	25,432
230	0.151	0.476	14,193	26,709
240	0.099	0.342	15,064	28,140
250	0.045	0.178	15,850	29,845
258.2	0.0	0.0	16,559	31,405

(c) The path $\overline{GE}$ in Fig. 3.26 denotes heating of 1 lbmole (0.454 kgmole) of liquid until 60 mole% has been vaporized. Terminals of tie line $\overline{DEF}$ are equilibrium vapor and liquid mole fractions. Heat added = 22,900 − 6164 = 16,736 Btu/lbmole (3.890×10^7 J/kgmole). □

References

1. Keyes, D. B., *Ind. Eng. Chem.*, **21**, 998–1001 (1929).
2. Keyes, D. B., U.S. Pat. 1,676,735, June 10, 1928.
3. Schreve, N., *Chemical Process Industries*, McGraw-Hill Book Co., New York, 1945, 659.
4. Edmister, W. C., and K. K. Okamoto, *Petroleum Refiner*, **38**, (8), 117–129 (1959).
5. Edmister, W. C., and K. K. Okamoto, *Petroleum Refiner*, **38**, (4), 271–280 (1959).
6. Taylor, D. L., and W. C. Edmister, *AIChE J.*, **17**, 1324–1329 (1971).
7. Janecke, E., *Z. Anorg. Allg. Chem.*, **51**, 132–157 (1906).
8. Francis, A. W., *Liquid–Liquid Equilibriums*, Interscience Publishing Co., New York, 1963.
9. Findlay, A., *Phase Rule*, Dover Publications, New York, 1951.

Problems

3.1 A liquid mixture containing 25 mole% benzene and 75 mole% ethyl alcohol, which components are miscible in all proportions, is heated at a constant pressure of 1 atm (101.3 kPa, 760 torr) from a temperature of 60°C to 90°C.

(a) At what temperature does vaporization begin?

(b) What is the composition of the first bubble of equilibrium vapor formed?

(c) What is the composition of the residual liquid when 25 mole% has evaporated? Assume that all vapor formed is retained within the apparatus and that it is completely mixed and in equilibrium with the residual liquid.

(d) Repeat Part (c) for 90 mole% vaporized.

(e) Repeat Part (d) if, after 25 mole% vaporized as in Part (c), the vapor formed is removed and an additional 35 mole% is vaporized by the same technique used in Part (c).

(f) Plot the temperature versus the percent vaporized for Parts (d) and (e).

Use the vapor pressure data below in conjunction with Raoult's and Dalton's laws to construct a *T*-*x*-*y* diagram, and compare it and the answers obtained in Parts (a) and (f) with those obtained using the experimental *T*-*x*-*y* data given below. What do you conclude?

Vapor pressure data

Vapor pressure, torr	20	40	60	100	200	400	760
Ethanol, °C	8	19.0	26.0	34.9	48.4	63.5	78.4
Benzene, °C	−2.6	7.6	15.4	26.1	42.2	60.6	80.1

Experimental *T*-*x*-*y* data for benzene–ethyl alcohol at 1 atm

Temperature, °C	78.4	77.5	75	72.5	70	68.5	67.7	68.5	72.5	75	77.5	80.1
Mole% benzene in vapor	0	7.5	28	42	54	60	68	73	82	88	95	100
Mole% benzene in liquid	0	1.5	5	12	22	31	68	81	91	95	98	100

3.2 Repeat Example 3.2 for the following liquid mixtures at 50°C.
(a) 50 mole% benzene and 50 mole% water.
(b) 50 mole% toluene and 50 mole% water.
(c) 40 mole% benzene, 40 mole% toluene, and 20 mole% water.

3.3 A gaseous mixture of 75 mole% water and 25 mole% *n*-octane at a pressure of 133.3 kPa (1000 torr) is cooled under equilibrium conditions at constant pressure from 136°C.
(a) What is the composition of the first drop to condense?
(b) What is the composition and temperature of the last part of the vapor to condense?
Assume water and *n*-octane are immiscible liquids.

3.4 Stearic acid is to be steam distilled at 200°C in a direct-fired still, heat jacketed to prevent condensation. Steam is introduced into the molten acid in small bubbles, and the acid in the vapor leaving the still has a partial pressure equal to 70% of the vapor pressure of pure stearic acid at 200°C. Plot the kilograms of acid distilled per kilogram of steam added as a function of total pressure from 101.3 kPa down to 3.3 kPa at 200°C. The vapor pressure of stearic acid at 200°C is 0.40 kPa.

3.5 The relative volatility, α, of benzene to toluene at 1 atm is 2.5. Construct an x-y diagram for this system at 1 atm. Repeat the construction using vapor pressure data for benzene from Problem 3.1 and for toluene from the table below in conjunction with Raoult's and Dalton's laws. Also construct a T-x-y diagram.
(a) A liquid containing 70 mole% benzene and 30 mole% toluene is heated in a container at 1 atm until 25 mole% of the original liquid is evaporated. Determine the temperature. The phases are then separated mechanically, and the vapors condensed. Determine the composition of the condensed vapor and the liquid residue.
(b) Calculate and plot the K-values as a function of temperature at 1 atm.

Vapor pressure of toluene

Vapor pressure, torr	20	40	60	100	200	400	760	1520
Temperature, °C	18.4	31.8	40.3	51.9	69.5	89.5	110.6	136

3.6 The vapor pressures of toluene and *n*-heptane are given in the accompanying tables.

Vapor pressure of *n*-heptane

Vapor pressure, torr	20	40	60	100	200	400	760	1520
Temperature, °C	9.5	22.3	30.6	41.8	58.7	78.0	98.4	124

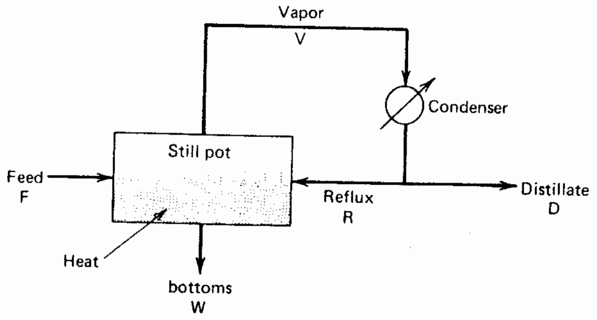
(a) Plot an x-y equilibrium diagram for this system at 1 atm by using Raoult's and Dalton's laws.
(b) Plot the T-x bubble-point curve at 1 atm.
(c) Plot α and K-values versus temperature.
(d) Repeat Part (a) using the arithmetic average value of α, calculated from the two extreme values.
(e) Compare your x-y and T-x-y diagrams with the following experimental data of Steinhauser and White [*Ind. Eng. Chem.*, **41**, 2912 (1949)].

Vapor–liquid equilibrium data for *n*-heptane/toluene at 1 atm

$x_{n\text{-heptane}}$	$y_{n\text{-heptane}}$	T, °C
0.025	0.048	110.75
0.129	0.205	106.80
0.250	0.349	104.50
0.354	0.454	102.95
0.497	0.577	101.35
0.692	0.742	99.73
0.843	0.864	98.90
0.940	0.948	98.50
0.994	0.993	98.35

3.7 Saturated liquid feed, at F = 40, containing 50 mole% A in B is supplied continuously to the apparatus below. The condensate from the condenser is split sot that half of it is returned to the still pot.
(a) If heat is supplied at such a rate that $W = 30$ and $\alpha = 2$, as defined below, what will be the composition of the overhead and the bottom product?
(b) If the operation is changed so that no condensate is returned to the still pot and $W = 3D$ as before, what will be the composition of the products?

$$\alpha = \text{relative volatility} = \frac{P_A^s}{P_B^s} = \frac{y_A x_B}{x_A y_B}$$



3.8 Vapor–liquid equilibrium data for mixtures of water and isopropanol at 1 atm (101.3 kPa, 760 torr) are given below.
(a) Prepare T-x-y and x-y diagrams.
(b) When a solution containing 40 mole% isopropanol is slowly vaporized, what will be the composition of the initial vapor formed?
(c) If this same 40% mixture is heated under equilibrium conditions until 75 mole% has been vaporized, what will be the compositions of the vapor and liquid produced?

Vapor–liquid equilibrium for isopropanol and water

T, °C	x	y
93.00	1.18	21.95
89.75	3.22	32.41
84.02	8.41	46.20
83.85	9.10	47.06
82.12	19.78	52.42
81.64	28.68	53.44
81.25	34.96	55.16
80.62	45.25	59.26
80.32	60.30	64.22
80.16	67.94	68.21
80.21	68.10	68.26
80.28	76.93	74.21
80.66	85.67	82.70
81.51	94.42	91.60

Notes: All compositions in mole% isopropanol.
Composition of the azeotrope: $x = y = 68.54\%$.
Boiling point of azeotrope: 80.22°C.
Boiling point of pure isopropanol: 82.5°C.

(d) Calculate K-values and α's at 80°C and 89°C.
(e) Compare your answers in Parts (a), (b), and (c) to those obtained from T-x-y and x-y diagrams based on the following vapor pressure data and Raoult's and Dalton's laws.

Vapor pressures of isopropanol and water

Vapor pressure, Torr	200	400	760
Isopropanol, °C	66.8	82	97.8
Water, °C	66.5	83	100

3.9 Forty-five kilograms of a solution containing 0.3 wt fraction ethylene glycol in water is to be extracted with furfural. Using Fig. 3.10a and 3.10e, calculate:
(a) Minimum quantity of solvent.
(b) Maximum quantity of solvent.
(c) The weights of solvent-free extract and raffinate for 45 kg solvent and the percent glycol extracted.
(d) The maximum possible purity of glycol in the finished extract and the maximum purity of water in the raffinate for one equilibrium stage.

3.10 Prove that in a triangular diagram, where each vertex represents a pure component, the composition of the system at any point inside the triangle is proportional to the length of the respective perpendicular drawn from the point to the side of the triangle opposite the vertex in question. It is not necessary to assume a special case (i.e., a right or equilateral triangle) to prove the above.

3.11 A mixture of chloroform ($CHCl_3$) and acetic acid at 18°C and 1 atm (101.3 kPa) is to be extracted with water to recover the acid.
(a) Forty-five kilograms of a mixture containing 35 wt% $CHCl_3$ and 65 wt% acid is treated with 22.75 kg of water at 18°C in a simple one-stage batch extraction. What are the compositions and weights of the raffinate and extract layers produced?
(b) If the raffinate layer from the above treatment is extracted again with one half its weight of water, what will be the compositions and weights of the new layers?
(c) If all the water is removed from this final raffinate layer, what will its composition be?
Solve this problem using the following equilibrium data to construct one or more of the types of diagrams in Fig. 3.10.

Liquid–liquid equilibrium data for $CHCl_3$–H_2O–CH_3COOH at 18°C and 1 atm

Heavy Phase (wt%)			Light Phase (wt%)		
$CHCl_3$	H_2O	CH_3COOH	$CHCl_3$	H_2O	CH_3COOH
99.01	0.99	0.00	0.84	99.16	0.00
91.85	1.38	6.77	1.21	73.69	25.10
80.00	2.28	17.72	7.30	48.58	44.12
70.13	4.12	25.75	15.11	34.71	50.18
67.15	5.20	27.65	18.33	31.11	50.56
59.99	7.93	32.08	25.20	25.39	49.41
55.81	9.58	34.61	28.85	23.28	47.87

3.12 Isopropyl ether (E) is used to separate acetic acid (A) from water (W). The liquid–liquid equilibrium data at 25°C and 1 atm (101.3 kPa) are given below.
(a) One hundred kilograms of a 30 wt% A-W solution is contacted with 120 kg of ether in an equilibrium stage. What are the compositions and weights of the

Liquid–liquid equilibrium data for acetic acid (A), water (W), and isopropanol ether (E) at 25°C and 1 atm

Water-Rich Layer			Ether-Rich Layer		
Wt% A	Wt% W	Wt% E	Wt% A	Wt% W	Wt% E
1.41	97.1	1.49	0.37	0.73	98.9
2.89	95.5	1.61	0.79	0.81	98.4
6.42	91.7	1.88	1.93	0.97	97.1
13.30	84.4	2.3	4.82	1.88	93.3
25.50	71.1	3.4	11.4	3.9	84.7
36.70	58.9	4.4	21.6	6.9	71.5
45.30	45.1	9.6	31.1	10.8	58.1
46.40	37.1	16.5	36.2	15.1	48.7

resulting extract and raffinate? What would be the concentration of acid in the (ether-rich) extract if all the ether were removed?

(b) A mixture containing 52 kg A and 48 kg W is contacted with 40 kg of E in each of 3 cross-flow stages. What are the raffinate compositions and quantities?

3.13 In its natural state, zirconium, which is an important material of construction for nuclear reactors, is associated with hafnium, which has an abnormally high neutron-absorption cross section and must be removed before the zirconium can be used. Refer to the accompanying flowsheet for a proposed liquid/liquid extraction process wherein tributyl phosphate (TBP) is used as a solvent for the separation of hafnium from zirconium. [R. P. Cox, H. C. Peterson, and C. H. Beyer, *Ind. Eng. Chem.*, **50** (2), 141 (1958).]

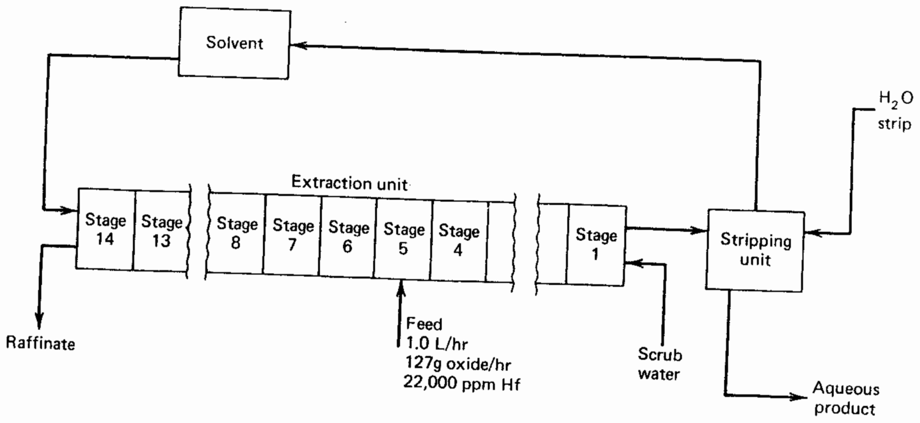
One liter per hour of 5.10 *N* HNO_3 containing 127 g of dissolved Hf and Zr oxides/liter is fed to stage 5 of a 14-stage extraction unit. The feed contains 22,000 ppm Hf. Fresh TBP enters stage 14 while scrub water is fed to stage 1. Raffinate is removed in stage 14, while the organic extract phase which is removed at stage 1 goes to a stripping unit. The stripping operation consists of a single contact between fresh water and the organic phase. The table below gives the experimental data obtained by Cox and coworkers. (a) Use these data to fashion a complete material balance for the process. (b) Check the data for consistency in as many ways as you can. (c) What is the advantage of running the extractor as shown? Would you recommend that all the stages be used?

Stagewise analyses of mixer-settler run

Stage	Organic Phase			Aqueous Phase		
	g oxide/liter	*N* HNO_3	$\frac{Hf}{Zr}(100)$	g oxide/liter	*N* HNO_3	$\frac{Hf}{Zr}(100)$
1	22.2	1.95	<0.010	17.5	5.21	<0.010
2	29.3	2.02	<0.010	27.5	5.30	<0.010
3	31.4	2.03	<0.010	33.5	5.46	<0.010
4	31.8	2.03	0.043	34.9	5.46	0.24
5	32.2	2.03	0.11	52.8	5.15	3.6
6	21.1	1.99	0.60	30.8	5.15	6.8
7	13.7	1.93	0.27	19.9	5.05	9.8
8	7.66	1.89	1.9	11.6	4.97	20
9	4.14	1.86	4.8	8.06	4.97	36
10	1.98	1.83	10	5.32	4.75	67
11	1.03	1.77	23	3.71	4.52	110
12	0.66	1.68	32	3.14	4.12	140
13	0.46	1.50	42	2.99	3.49	130
14	0.29	1.18	28	3.54	2.56	72
Stripper	.....	0.65	....	76.4	3.96	<0.01

[From R. P. Cox, H. C. Peterson, and C. H. Beyer, *Ind. Eng. Chem.*, **50** (2), 141 (1958).]

(Problem 3.13 is adapted from E. J. Henley and H. Bieber, *Chemical Engineering Calculations*, McGraw-Hill Book Co., p. 298, 1959).



3.14 Repeat Example 3.8 for each of the following changes.

(a) Two kilograms of pure benzene is mixed with 1 kg of meal containing 50 wt% oil.

(b) One kilogram of pure benzene is mixed with 1 kg of meal containing 25 wt% oil.

3.15 At 25°C and 101 kPa, 2 gmoles of a gas containing 35 mole% propylene in propane is equilibrated with 0.1 kg of silica gel adsorbent. Using the equilibrium data of Fig. 3.21, calculate the gram-moles and composition of the gas adsorbed and the equilibrium composition of the gas not adsorbed.

3.16 Vapor–liquid equilibrium data for the system acetone–air–water at 1 atm (101.3 kPa) are given as:

y, mole fraction acetone in air	0.004	0.008	0.014	0.017	0.019	0.020
x, mole fraction acetone in water	0.002	0.004	0.006	0.008	0.010	0.012

(a) Plot the data as (1) a graph of moles acetone/mole air versus moles acetone/mole water, (2) partial pressure of acetone versus g acetone/g water, (3) y versus x.

(b) If 20 moles of gas containing 0.015 mole fraction acetone is brought into contact with 15 moles of water in an equilibrium stage, what would be the composition of the discharge streams? Solve graphically.

(Problem 3.16 is adapted from E. J. Henley and H. K. Staffin, *Stagewise Process Design*, J. Wiley & Sons, New York, 1963.)

3.17 It has been proposed that oxygen be separated from nitrogen by absorbing and desorbing air in water. Pressures from 101.3 to 10,130 kPa and temperatures between 0 and 100°C are to be used.

(a) Devise a workable scheme for doing the separation assuming the air is 79 mole% N_2 and 21 mole% O_2.

(b) Henry's law constants for O_2 and N_2 are given in Fig. 3.23. How many batch absorption steps would be necessary to make 90 mole% pure oxygen? What yield of oxygen (based on total amount of oxygen feed) would be obtained?

3.18 A vapor mixture having equal volumes of NH_3 and N_2 is to be contacted at 20°C and 1 atm (760 torr) with water to absorb a portion of the NH_3. If 14 m^3 of this mixture is brought into contact with 10 m^3 of water and if equilibrium is attained, calculate the percent of the ammonia originally in the gas that will be absorbed. Both temperature and total pressure will be maintained constant during the absorption. The partial pressure of NH_3 over water at 20°C is:

Partial Pressure of NH_3 in air, torr	*Grams of Dissolved NH_3/100 g of H_2O*
470	40
298	30
227	25
166	20
114	15
69.6	10
50.0	7.5
31.7	5.0
24.9	4.0
18.2	3.0
15.0	2.5
12.0	2.0

3.19 Using the y-x and T-x-y diagrams constructed in Problem 3.5 and the enthalpy data provided below,

(a) Construct an H-x-y diagram for the benzene–toluene system at 1 atm (101.3 kPa). Make any assumptions necessary.

	Saturated Enthalpy, kJ/kg			
	Benzene		**Toluene**	
***T*, °C**	H_L	H_V	H_L	H_V
60	79	487	77	471
80	116	511	114	495
100	153	537	151	521

(b) Calculate the energy required for 50 mole% vaporization of a 30 mole% liquid solution of benzene and toluene initially at saturation temperature. If the vapor is then condensed, what is the heat load on the condenser if the condensate is saturated and if it is subcooled by 10°C?

3.20 It is required to design a fractionation tower to operate at 101.3 kPa to obtain a distillate consisting of 95 mole% acetone (A) and 5 mole% water, and a residue containing 1 mole% A. The feed liquid is at 125°C and 687 kPa and contains 57 mole% A. The feed is introduced to the column through an expansion valve so that it enters the column partially vaporized at 60°C. Construct an H-x-y diagram and determine the molar ratio of liquid to vapor in the partially vaporized feed. Enthalpy and equilibrium data are as follows.

Molar latent heat of A = 29,750 kJ/kgmole (assume constant)

Molar latent heat of H_2O = 42,430 kJmole (assume constant)
Molar specific heat of liquid A = 134 kJ/kgmole · °K
Molar specific heat of liquid H_2O = 75.3 kJ/kgmole · °K
Enthalpy of high-pressure, hot feed before adiabatic expansion = 0
Enthalpies of feed phases after expansion: H_V = 27,200 kJ/kgmole
H_L = −5270 kJ/kgmole

Vapor–liquid equilibrium data for acetone–H_2O at 101.3 kPa

	***T*, °C**						
	56.7	**57.1**	**60.0**	**61.0**	**63.0**	**71.7**	**100**
Mole% A in liquid	100	92.0	50.0	33.0	17.6	6.8	0
Mole% A in vapor	100	94.4	85.0	83.7	80.5	69.2	0