Quiz 11
Chemical Engineering Thermodynamics
April 16, 2015

1)
10.10 Solvent vessels must be purged before maintenance personnel enter in order to ensure that: (1) sufficient oxygen is available for breathing; (2) vapor concentrations are below the flash point; (3) vapor concentrations are below the Occupational Safety and Health Administration (OSHA) limits if breathing apparatus is not to be used. Assuming that a 8 m^3 fixed-roof solvent tank has just been drained of all liquid and that the vapor phase is initially saturated at 22°C, estimate the length of purge necessary with 2 m^3/min of gas at 0.1 MPa and 22°C to reach the OSHA 8-hr exposure limit.[13]

(a) Hexane 500 ppm

See equations/tables below.

2)
10.11 A pharmaceutical product is crystallized and washed with absolute ethanol. A 100 kg batch of product containing 10% ethanol by weight is to be dried to 0.1% ethanol by weight by passing 0.2 m^3/min of 50°C nitrogen through the dryer. Estimate the rate (mol/min) that ethanol is removed from the crystals, assuming that ethanol exerts the same vapor pressure as if it were pure liquid. Based on this assumption, estimate the residence time for the crystals in the dryer. The dryer operates at 0.1 MPa and the vapor pressure of the pharmaceutical is negligible.

See equations/tables below.

3)
10.12 Benzyl chloride is manufactured by the thermal or photochemical chlorination of toluene. The chlorination is usually carried out to no more than 50% toluene conversion to minimize the benzal chloride formed. Suppose reactor effluent emissions can be modeled ignoring by-products, and the effluent is 50 mol% toluene and 50 mol% benzyl chloride. Estimate the emission of toluene and benzyl chloride (moles of each) when an initially empty 4 m^3 holding tank is filled with the reactor effluent at 30°C and 0.1 MPa.

See equations/tables below.

$$y_i^f = y_i^i \exp\left(\frac{-\dot{V}_{sweep}}{\underline{V}_{tank}} t\right) \qquad 10.27$$

R = 8.314 MPa cm^3/(mole K°)

Hexane 86.18 g/mole *Toluene 92.14 g/mol*

Ethanol 46.07 g/mol *Benzyl chloride 126.6 g/mol*

PROPERTIES OF SELECTED COMPOUNDS

Heat capacities are values for ***ideal gas at 298 K*** *and should be used for* ***order of magnitude calculations*** *only. See appendices for temperature-dependent formulas and constants.*

ID	Compound	T_c (K)	P_c (MPa)	ω	ρ g/cm³	MW	C_P^{ig}/R	δ (J/cm³)^½	α (J/cm³)^½	β (J/cm³)^½
Aliphatics										
1	METHANE	190.6	4.604	0.011	*0.29*	16	4.30	11.7	0	0
2	ETHANE	305.4	4.880	0.099	*0.43*	30	6.31	13.5	0	0
3	PROPANE	369.8	4.249	0.152	*0.58*	44	8.85	13.1	0	0
4	*n*-BUTANE	425.2	3.797	0.193	*0.60*	58	11.89	13.5	0	0
5	ISOBUTANE	408.1	3.648	0.177	*0.55*	58	11.70	12.5	0	0
7	*n*-PENTANE	469.7	3.369	0.249	0.62	72	14.45	14.3	0	0
8	ISOPENTANE	460.4	3.381	0.228	0.62	72	14.28	13.9	0	0
9	NEOPENTANE	433.8	3.199	0.196	0.60	72	14.62	13.1	0	0
11	*n*-HEXANE	507.4	3.012	0.305	0.66	86	17.21	14.9	0	0
17	*n*-HEPTANE	540.3	2.736	0.349	0.68	100	19.95	15.3	0	0
27	*n*-OCTANE	568.8	2.486	0.396	0.70	114	22.70	15.5	0	0
27	ISOOCTANE	544.0	2.570	0.303	0.70	114	22.50	14.1	0	0
46	*n*-NONANE	595.7	2.306	0.437	0.71	128	25.45	15.6	0	0
56	*n*-DECANE	618.5	2.123	0.484	0.73	142	28.22	15.7	0	0
64	*n*-DODECANE	658.2	1.824	0.575	0.75	170	33.71	15.9	0	0
66	*n*-TETRADECANE	696.9	1.438	0.570	0.76	198	39.22	16.1	0	0
68	*n*-HEXADECANE	720.6	1.419	0.747	0.77	226	44.54	16.2	0	0

E.3 ANTOINE CONSTANTS

The following constants are for the equation

$$\log_{10} P^{sat} = A - \frac{B}{T + C}$$

where P^{sat} is in mmHg, and T is in Celsius. Additional Antoine constants are tabulated in Antoine.xls.

	A	*B*	*C*	*T* range (°C)	Source
Acetic acid	8.02100	1936.01	258.451	18–118	a
Acetic acid	8.26735	2258.22	300.97	118–227	a
Acetone	7.63130	1566.69	273.419	57–205	a
Acetone	7.11714	1210.595	229.664	−13–55	a
Acrolein (2-propenal)	8.62876	2158.49	323.36	2.5–52	b
Benzene	6.87987	1196.76	219.161	8–80	a
Benzyl chloride	7.59716	1961.47	236.511	22–180	b
Biphenyl (solid)	13.5354	4993.37	296.072	20–40	c
1-Butanol	7.81028	1522.56	191.95	30–70	d
1-Butanol	7.75328	1506.07	191.593	70–120	d
2-Butanone	7.28066	1434.201	246.499	−6.5–80	b
Chloroform	6.95465	1170.966	226.232	−10–60	a
Ethanol	8.11220	1592.864	226.184	20–93	a
Hexane	6.91058	1189.64	226.28	−30–170	a
1-Propanol	8.37895	1788.02	227.438	−15–98	a
2-Propanol	8.87829	2010.33	252.636	−26–83	a
Methanol	8.08097	1582.271	239.726	15–84	a
Naphthalene (solid)	8.62233	2165.72	198.284	20–40	e
Pentane	6.87632	1075.78	233.205	−50–58	a
3-Pentanone	7.23064	1477.021	237.517	36–102	a
Toluene	6.95087	1342.31	219.187	−27–111	a
Water	8.07131	1730.63	233.426	1–100	a

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(a) Hexane 500 ppm

(10.10) Solvent vessels must be purged...

	hexane	1-butanol	chloroform	ethanol	toluene
A	6.87601	7.81028	6.95465	8.1122	6.95087
B	1171.17	1522.56	1170.966	1592.864	1342.31
C	224.408	191.95	226.232	226.184	219.187
tMin[°C]	-25	30	-10	20	-27
tMax[°C]	92	70	60	93	111
T(C)	22	22	22	22	22
Psat(mmHg)	132.7515	4.94141	172.7531	49.44508	24.29055
yi = Psat/750	0.177002	0.006589	0.230337	0.065927	0.032387
Yf	5.00E-04	1.00E-04	5.00E-05	1.00E-03	2.00E-04
t(min)	23.47723	16.75167	33.74111	16.75418	20.34883

2)

10.11 A pharmaceutical product is crystallized and washed with absolute ethanol. A 100 kg batch of product containing 10% ethanol by weight is to be dried to 0.1% ethanol by weight by passing 0.2 m^3/min of 50°C nitrogen through the dryer. Estimate the rate (mol/min) that ethanol is removed from the crystals, assuming that ethanol exerts the same vapor pressure as if it were pure liquid. Based on this assumption, estimate the residence time for the crystals in the dryer. The dryer operates at 0.1 MPa and the vapor pressure of the pharmaceutical is negligible.

(10.11) A pharmaceutical product is crystallized...

This is a semi-batch process. Crystals stay in dryer while gas passes through.

Volumetric flow rate of nitrogen $\underline{\dot{V}} = 0.2 m^3/min$

So molar flow rate $\dot{n}_{N_2}$ would be $\frac{P\underline{\dot{V}}}{RT} = (0.1 \cdot 0.2 \cdot 10^6)/(8.314 \cdot 323.15)$

= 7.444 moles/min

The saturation vapor pressure of the ethanol can be calculated using the Antoine equation

$\log_{10} P^{sat} = 8.1122 - \frac{1592.864}{226.184 + 50}$ which gives $P^{sat} = 221 mmHg = 0.291$ bar

Since the total pressure of the gases in the downstream of the drying process would be sum of the partial pressures of the EtOH and N_2 $P_{total} = P_{EtOH} + P_{N2}$ and the ratio of partial pressure is the mole fraction y_i of the gas in the stream.

Hence we can write

$$\dot{n}_{EtOH} = \frac{y_{EtOH}}{y_{N_2}}\dot{n}_{N_2} = \dot{n}_{EtOH} = \frac{P^{sat}_{EtOH}(bars)}{P - P^{sat}_{EtOH}(bars)}\dot{n}_{N_2} = \frac{0.291}{1-0.291}7.444 = 3.0523\,\frac{\text{moles}}{\text{min}}$$

Basis: 100 kg wet crystals, 90 kg dry crystals, 10 kg EtOH

Initial moles of EtOH in the product $n^{i}_{EtOH} = \frac{10000\text{grams}}{46\text{grams/mole}} = 217.39$ moles

Final moles of EtOH in the product, $0.001 = m_{EtOH}/(90000 + m_{EtOH}) \rightarrow m_{EtOH} = 90.1$ g

Final moles of EtOH in the product $n^{f}_{EtOH} = \frac{90.1\text{grams}}{46\text{grams/mole}} = 1.96$ moles

$\Delta n = 217.39 - 1.96 = 215.43$ moles per 100kg feed

So the time for drying = 215.43 mol/3.0523(mol/min) = 70.57 minutes
So the flowrate of wet crystals into the dryer is 100 kg/70.6 min = 1.42 kg/min

3)

10.12 Benzyl chloride is manufactured by the thermal or photochemical chlorination of toluene. The chlorination is usually carried out to no more than 50% toluene conversion to minimize the benzal chloride formed. Suppose reactor effluent emissions can be modeled ignoring by-products, and the effluent is 50 mol% toluene and 50 mol% benzyl chloride. Estimate the emission of toluene and benzyl chloride (moles of each) when an initially empty 4 m^3 holding tank is filled with the reactor effluent at 30°C and 0.1 MPa.

(10.12) Benzyl chloride is manufactured...

Initial head volume of the tank : $V^{i}_{head} = 4.0\ m^3$
Final head volume of the tank : $V^{f}_{head} = 0.0\ m^3$
Temperature: 303.15 K

Using ideal gas equation
$n^{i}_{head} = PV^{i}_{head}/RT$ and $n^{f}_{head} = PV^{f}_{head}/RT$
and the Raoult's law
$y_i = x_i P_i^{sat}/P = x_i K_i$
we have $n^{i}_{head} = 0.1 \cdot 4/(8.314 \cdot 10^{-6} \cdot 303.15) = 158.7$ moles, $n^{f}_{head} = 0$ moles

Using Antoine equation
$P^{sat} = 10^{[6.95087 - 1342.31/(30+219.19)]} = 37\text{mmHg}$ for toluene
$P^{sat} = 10^{[7.597156 - 1961.47/(30+236.51)]} = 1.727$ mmHg for benzyl chloride
$K_{toluene} = 37/760 = 0.0487$, $K_{benzyl\ chloride} = 1.727/760 = 0.00227$
$y_{toluene} = 0.5 \cdot (0.0487) = 0.02435$, $y_{benzyl\ chloride} = 0.5 \cdot (0.00227) = 0.001136$
so $\Delta n_{toluene} = 0.02435 \cdot (158.7 - 0) = 3.864$ moles
& $\Delta n_{benzylchloride} = 0.001136 \cdot (158.7 - 0) = 0.1803$ moles