Quiz 3
Chemical Engineering Thermodynamics
February 4, 2016

3.7. Benzene and benzyl chloride produced from the reaction described in problem 3.6 are separated by distillation at 1 bar. The chlorine and HCl are removed easily and this problem concerns only a binary mixture. Suppose the liquid flow to the reboiler is 90 mol% chlorobenzene and 10 mol% benzene at 121.9°C. The boilup ratio is 0.7 at 127.8°C, and the vapor leaving the reboiler is 12.7 mol% benzene. The heat of vaporization of chlorobenzene is 41 kJ/mol. Heat capacities for liquids are in problem 3.6(a). Determine the heat duty for the reboiler.

In answering this, sketch the process, do a mass balance, and an energy balance.

(*see problem 3.6 and tables below for parameters you need for the calculations*)

3.6. Chlorobenzene$_{(l)}$ is produced by reacting benzene$_{(l)}$ initially at 30°C with $Cl_{2(g)}$ initially at 30°C in a batch reactor using $AlCl_3$ as a catalyst. $HCl_{(g)}$ is a by-product. During the course of the reaction, the temperature increases to 50°C. To avoid dichlorobenzenes, conversion of benzene is limited to 30%. The NIST WebBook reports the heats of formation for liquid benzene and chlorobenzene at 25°C as 49 kJ/mol and 11.5 kJ/mol, respectively. The heat capacities of liquid benzene and chlorobenzene are 136 J/mol-K and 150 J/mol-K, respectively.

		$\Delta H_{f,298.15}$	$\Delta G_{f,298.15}$	Heat Capacity Constants			
		kJ/mol	kJ/mol	A	B	C	D
Ideal gases: Standard State: Ideal Gas 298.15 K and 1 bar. [c] USE PRESSURE IN BAR WHEN USING THESE PROPERTIES							
260	1-Decene	-124.69	119.83				
270	Cyclohexene	-4.6	106.859				
303	1,3-Butadiene	109.24	149.73	-1.687	0.3419	-2.340E-04	6.335E-08
309	2-Methyl-1,3-butadiene (Isoprene)			-3.412	0.4585	-3.337E-04	1.000E-07
401	Acetylene	226.731	209.2	26.82	0.07578	-5.007E-05	1.412E-08
	Styrene			-28.25	0.6159	-4.023E-4	9.935E-8
Aromatics							
501	Benzene	82.88	129.75	-33.92	0.4739	-3.017E-04	7.130E-08
502	Toluene	50.17	122.29	-24.35	0.5125	-2.765E-04	4.911E-08
504	Ethylbenzene	29.92	130.73	-43.1	0.7072	-4.811E-04	1.301E-07
505	1,2-Dimethyl benzene	19	122.22	-15.85	0.5962	-3.443E-04	7.528E-08
506	1,3-Dimethyl benzene	17.24	119	-29.17	0.6297	-3.747E-04	8.478E-08
507	1,4-Dimethyl benzene	17.95	121.26	-1.509	0.6042	-3.374E-04	6.820E-08
510	Isopropylbenzene (Cumene)	3.93	137.15	-33.936	0.7842	-5.087E-04	1.291E-07
558	Biphenyl	182.42	281.08	-97.07	1.106	-8.855E-04	2.790E-07
601	Phenylethene	147.36	213.802				
701	Naphthalene	150.959	223.593	-68.8	0.8499	-6.506E-04	1.981E-07
702	1-Methylnaphthalene			-64.82	0.9387	-6.942E-04	2.016E-07
706	1,2,3,4-Tetrahydro-naphthalene (Tetralin)	24.2	167.1				
803	Indene	163.28	233.97				
805	Phenanthrene	206.9	308.1				
Oxygenated Hydrocarbons							
1001	Formaldehyde	-117.152	-112.968				
1002	Acetaldehyde	-166.021	-133.302				
1051	Acetone	-215.7	-151.2	6.301	0.2606	-1.253E-04	2.038E-08
1052	2-Butanone	-239	-151.9	10.94	0.3559	-1.900E-04	3.920E-08
1101	Methanol	-200.94	-162.24	21.15	0.07092	2.587E-05	-2.852E-08
1102	Ethanol	-234.95	-167.73	9.014	0.2141	-8.390E-05	1.373E-09
1103	Propanol	-255.2	-161.795	2.47	0.3325	-1.855E-04	4.296E-08
1104	2-Propanol	-272.295	-173.385	32.43	0.1885	6.406E-05	-9.261E-08
1105	Butanol	-274.6	-150.666	3.266	0.418	-2.242E-04	4.685E-08
1107	Isobutanol			-7.708	0.4689	-2.884E-04	7.231E-08
1114	1-Hexanol	-316.5	-135.562				

E.2. Latent Heats

	T_m(°C)	ΔH^{fus} kJ/mol	T^{sat}(°C) at 1.01325 bar	ΔH^{vap} kJ/mol
Acetic acid	16.6	12.09	118.2	23.7
Acetone	–95.	5.69	56.	30.2
Anthracene	216.5	28.86		
Benzene	5.53	9.837	80.1	30.765
Biphenyl	69.2	18.58		
n-Butane	–138.3	4.661	–0.6	22.305
Cyclohexane	6.7	2.677		
Ethanol	–114.6	5.021	78.5	38.58
n-Hexane	–95.32	13.03	68.74	28.85
Naphthalene	80.2	18.80		
Phenanthrene	99.2	16.46		
Phenol	40.9	11.43		
Water	0.00	6.0095	100.0	40.656

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/cm^3	MW	C_P^{ig}/R	δ (J/cm^3)$^{1/2}$	α (J/cm^3)$^{1/2}$	β (J/cm^3)$^{1/2}$
Olefins and Acetylene										
201	ETHYLENE	282.4	5.032	0.085	*0.43*	28	5.26	13.5	0	0.40
202	PROPYLENE	364.8	4.613	0.142	*0.61*	42	7.69	13.2	0	0.40
207	1-BUTENE	419.6	4.020	0.187	*0.63*	56	10.31	13.7	0	0.40
204	ISOBUTENE	417.9	3.999	0.189	*0.59*	56	10.72	13.7	0	0.40
209	1-PENTENE	464.8	3.529	0.233	0.63	70	13.17	14.5	0	0.24
401	ACETYLENE	308.3	6.139	0.187	*0.50*	28	5.32	*18.68*	0.40	0.40
303	1,3-BUTADIENE	425.4	4.330	0.193	*0.65*	54	9.56	15.6	0	0.70
309	ISOPRENE	484	3.850	0.158	0.68	68	12.78	15.3	0	0.70
Aromatics										
501	BENZENE	562.2	4.898	0.211	0.87	78	9.82	18.7	0.63	2.24
502	TOLUENE	591.8	4.109	0.264	0.86	92	12.49	18.3	0.57	2.23
504	ETHYLBENZENE	617.2	3.609	0.304	0.86	106	15.44	18.0	0.23	1.83
505	*o*-XYLENE	630.4	3.734	0.313	0.88	106	16.03	18.4	0.10	1.80
506	*m*-XYLENE	617.1	3.541	0.326	0.86	106	15.35	18.1	0.19	1.84
507	*p*-XYLENE	616.3	3.511	0.326	0.86	106	15.26	17.9	0.27	1.87
510	CUMENE	631.2	3.209	0.338	0.86	121	18.25	17.4	0.20	2.57
558	BIPHENYL	789.3	3.847	0.366	0.99	154	19.52	19.3	0.50	4.00
563	DIPHENYLMETHANE	768	2.920	0.461	1.00	168	21.87	19.6	0.50	4.00
701	NAPHTHALENE	748.4	4.051	0.302	*0.98*	128	16.03	19.5	0.86	6.87
702	METHYLNAPHTHALENE	772	3.650	0.292	1.02	142	19.08	20.1	0.77	6.13
706	TETRALIN	720.2	3.300	0.286	0.97	132	18.63	19.3	0.60	4.82

Chloro Benzenchlorobenzene

Thermodynamic properties [edit]

Phase behavior	
Triple point	? K (? °C), ? Pa
Critical point	633.4 K (360.25°C), 4.52 MPa
Std enthalpy change of fusion, $\Delta_{fus}H^{\ominus}$	? kJ/mol
Std entropy change of fusion, $\Delta_{fus}S^{\ominus}$	9.6 J/(mol·K)
Std enthalpy change of vaporization, $\Delta_{vap}H^{\ominus}$	40.97 kJ/mol
Std entropy change of vaporization, $\Delta_{vap}S^{\ominus}$	? J/(mol·K)
Solid properties	
Std enthalpy change of formation, $\Delta_f H^{\ominus}_{solid}$	? kJ/mol
Standard molar entropy, $S^{\ominus}_{solid}$	? J/(mol K)
Specific heat capacity, c_p	? J/(mol K)
Liquid properties	
Std enthalpy change of formation, $\Delta_f H^{\ominus}_{liquid}$	11.1 kJ/mol
Standard molar entropy, $S^{\ominus}_{liquid}$	? J/(mol K)
Specific heat capacity, c_p	150.1 J/(mol K)
Gas properties	
Std enthalpy change of formation, $\Delta_f H^{\ominus}_{gas}$	52.0 kJ/mol
Standard molar entropy, $S^{\ominus}_{gas}$	? J/(mol K)
Specific heat capacity, c_p	? J/(mol K)
Van der Waals' constants	a = 25.8 L^2bar/mol^2 b = 0.1454 L/mol
Other properties	
Std molar enthalpy of hydration of gas, $\Delta_{hyd}H^{\infty} = \Delta_{sol}H^{\infty} - \Delta_{vap}H^{\ominus}$	-30.6 kJ/mol @ 298.15K

Answers **Quiz 3**

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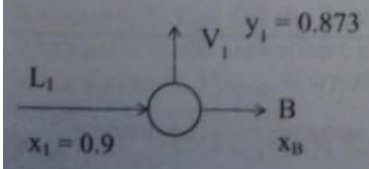
(3.07) Benzene and benzyl chloride produced from …



Material balance to find x_B. Material balance on ΦCl using a basis L_1 = 1 mol/min.

$L_1(0.9) - V_1(0.873) = B(x_{\Phi Cl})_B$

$[1(0.9) - 0.7(0.873)]/0.3 = (x_{\Phi Cl})_B = 0.963$

Energy Balance

$0 = H_{L1}L_1 - H_{V1}V_1 - H_BB + Q$

Solution for enthalpies will use method of Fig 2.6(a)

Reference State- Liquid at 121.9K

$H_L = Cp_L(T-T_R)$

$H_V = Cp_L(T_B-T_R) + \Delta H^{vap} + Cp_V(T_{V1}-T_B)$

Note that T_R is above T_B for benzene so the first term for Hv will be negative. Use ideal solution approximation, $Hv = y_1Hv_1 + y_2Hv_2$, etc. From the NIST webbook, T_B for chlorobenzene is 404.9K. Tabulating calculations for each stream in columns to the left, using the pure component properties tabulated in the right columns, the stream enthalpies are calculated below.

	L1	V1	B
flow	1	0.7	0.3
T(K)	395.05	400.95	400.95
x(Φ)	0.1	0.127	0.127
x(ΦCl)	0.9	0.873	0.873
HL			
(Φ)	0		802.4
(ΦCl)	0		885
HL(for V)(J/mol)			
(Φ)		-5684.8	
(ΦCl)		1477.5	
ΔHvap(kJ/mol)			
(Φ)		30.765	
(ΦCl)		41	
HV(J/mol)			
(Φ)		5040.277	
(ΦCl)		-509.198	
Htotal(J/mol)			
(Φ)		30120.48	
(ΦCl)		41968.3	

Benzene	Chlorobenzene
CpL(J/mol-K)	
136	150
ΔHvap(kJ/mol)	
30.765	41
CpV(J/mol-K) constants	
-33.92	-33.89
0.4739	0.5631
-3.02E-04	-4.52E-04
7.13E-08	1.43E-07
Tb(K)	
353.25	404.9

Insert values into energy balance

$Q = H_{V1}V_1 + H_BB - H_{L1}L_1$

$Q = \{0.873(41968.3)+0.127(30120)\}(0.7) + \{0.963(885)+0.037(802.4)\}(0.3) - \{0\}(1)$

$= 40464$ J/mol * 0.7 mol/(mol L_1) + 882 J/mol * 0.3 mol/(mol L_1) = 28590 J/(mol L_1).

The heat requirement per mole of L_1 is 28590 J/(mol L_1)