EN727005

THERMODYNAMICS FOR CHEMICAL ENGINEERS

อุณหพลศาสตร์สำหรับวิศวกรเคมี

Chapter 6

Thermodynamic Properties of fluids

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6.7 GENERALIZED PROPERTY CORRELATION FOR GASES

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \ldots(6.46) \qquad \frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \quad (const\ T) \quad \ldots(6.48)$$

$$P = P_c P_r \rightarrow dP = P_c dP_r, \quad T = T_c T_r \rightarrow dT = T_c dT_r$$

substitue into Eqs.(6.46) *and* (6.48):

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \quad \ldots(6.83)$$

$$\frac{S^R}{R} = T_r \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z-1)\frac{dP_r}{P_r} \quad \ldots(6.84)$$

$$Z = Z^0 + \omega Z^1 \xrightarrow{\text{diff}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + \omega\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r}$$

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \quad \ldots(6.83)$$

$$Eq.(6.83): \frac{H^R}{RT_c} = \underbrace{\left[-T_r^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}\right]} - \omega \underbrace{\left[T_r^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}\right]}$$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega\frac{(H^R)^1}{RT_c} \quad \ldots(6.85)$$

$$\frac{S^R}{R} = T_r \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z-1)\frac{dP_r}{P_r} \quad \ldots(6.84)$$

$$Eq.(6.84): \frac{S^R}{R} = \underbrace{\left[-\int_0^{P_r} \left\langle T_r\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} + Z^0 - 1\right\rangle \frac{dP_r}{P_r}\right]} - \omega \underbrace{\left[\int_0^{P_r} \left\langle T_r\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} + Z^1\right\rangle \frac{dP_r}{P_r}\right]}$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega\frac{(S^R)^1}{R} \quad \ldots(6.86)$$

Table E.5 - E.12

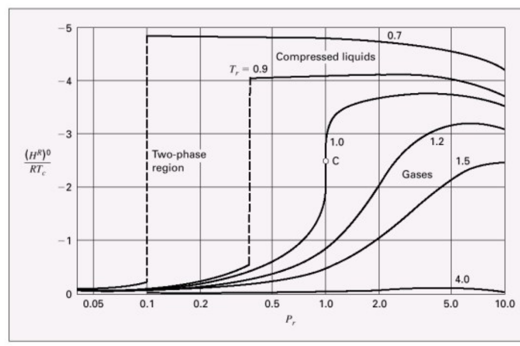


Figure 6.5: The Lee/Kesler correlation for $(H^R)^0/RT_c$ as a function of T_r and P_r.

Analytical correlation of the residual properties at low pressure

The generalized second-virial-coefficient correlation forms

$$\hat{B} = \frac{BP_c}{RT_c} = \boxed{\quad}, \qquad \frac{d\hat{B}}{dT_r} = \frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}$$

$$\frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right) \ldots(6.55) \qquad \frac{S^R}{R} = -\frac{P}{R}\frac{dB}{dT} \quad \ldots(6.56)$$

$$Eqs.(6.55)\ and\ (6.56); \quad \frac{H^R}{RT_c} = P_r\left(\hat{B} - T_r\frac{d\hat{B}}{dT_r}\right), \qquad \frac{S^R}{R} = -P_r\frac{d\hat{B}}{dT_r}$$

$$\Rightarrow \frac{H^R}{RT_c} = P_r\left[B^0 - T_r\frac{dB^0}{dT_r} + \omega\left(B^1 - T_r\frac{dB^1}{dT_r}\right)\right] \quad \ldots(6.87)$$

$$\frac{S^R}{R} = -P_r\left(\frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}\right) \quad \ldots(6.88)$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \ldots(3.65)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad \ldots(3.66)$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad \ldots(6.89)$$

$$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \quad \ldots(6.90)$$

H^R and S^R with ideal-gas heat capacities

- For a change from state 1 to 2:

$$H_2 = H_0^{ig} + \int_0^{T_2} C_P^{ig} dT + H_2^R \qquad H_1 = H_0^{ig} + \int_0^{T_1} C_P^{ig} dT + H_1^R$$

- The enthalpy change for the process, $\Delta H = H_2 - H_1$

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig} dT + H_2^R - H_1^R \quad \ldots(6.91)$$

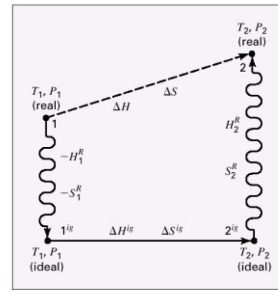
$$Similarly, \ \Delta S = \int_{T_1}^{T_2} C_P^{ig} dT - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R \quad \ldots(6.92)$$

- Alternative form

$$\Delta H = \left\langle C_P^{ig} \right\rangle_H (T_2 - T_1) + H_2^R - H_1^R \quad \ldots(6.93)$$

$$\Delta S = \left\langle C_P^{ig} \right\rangle_S \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R \quad \ldots(6.94)$$

Figure 6.6: Calculational path for property changes ΔH and ΔS.



A three-step calculational path

- Step 1→1^{ig}: A hypothetical process that transforms a real gas into an ideal gas at T_1 and P_1.

$$H_1^{ig} - H_1 = -H_1^R \qquad S_1^{ig} - S_1 = -S_1^R$$

- Step 1^{ig} →2^{ig}: Changes in the ideal-gas state from (T_1,P_1) to (T_2,P_2).

$$\Delta H^{ig} = H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT \quad \ldots(6.95)$$

$$\Delta S^{ig} = S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} \ldots(6.96)$$

- Step 2^{ig} →2: Another hypothetical process that transform the ideal gas back into a real gas at T_2 and P_2.

$$H_2 - H_2^{ig} = H_2^R \qquad S_2 - S_2^{ig} = S_2^R$$

Ex. 6.9

Estimate V, U, H and S for 1-butane vapor at 200°C, 70 bar if H and S are set equal to zero for saturated liquid at 0°C.

Assume: T_c=420.0 K, P_c=40.43 bar, T_n=266.9 K, ω=0.191

$C_p^{ig}/R=1.967+31.630\times10^{-3}T-9.837\times10^{-6}T^2$ (T/K)

Solution

$$T_r = \frac{200+273.15}{420.0} = 1.127 \qquad P_r = \frac{70}{40.43} = 1.731$$

$$Eq.(3.57) \ and \ Table \ E.3 \ and \ E.4;$$

$$Z = Z^0 + \omega Z^1 = 0.485 + 0.191(0.142) = 0.512$$

$$V = \frac{ZRT}{P} = \frac{0.512(83.14)(473.15)}{70} = 287.8 \ cm^3 mol^{-1}$$

Table E.3: Values of Z^0

P_r = 1.731

T_r = 1.127

P_r = / T_r	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
0.30	0.2892	0.3479	[illegible]	[illegible]	0.8648	1.4366	2.0048	2.8507
0.35	0.2604	0.3123	0.3901	0.5195	0.7775	1.2902	1.7987	2.5539
0.40	0.2379	0.2853	0.3563	0.4744	0.7095	1.1758	1.6373	2.3211
0.45	0.2200	0.2638	0.3294	0.4384	0.6551	1.0841	1.5077	2.1338
0.50	0.2056	0.2465	0.3077	0.4092	0.6110	1.0094	1.4017	1.9801
0.55	0.1939	0.2323	0.2899	0.3853	0.5747	0.9475	1.3137	1.8520
0.60	0.1842	0.2207	0.2753	0.3657	0.5446	0.8959	1.2398	1.7440
0.65	0.1765	0.2113	0.2634	0.3495	0.5197	0.8526	1.1773	1.6519
0.70	0.1703	0.2038	0.2538	0.3364	0.4991	0.8161	1.1341	1.5729
0.75	0.1656	0.1981	0.2464	0.3260	0.4823	0.7854	1.0787	1.5047
0.80	0.1626	0.1942	0.2411	0.3182	0.4690	0.7598	1.0400	1.4456
0.85	0.1614	0.1924	0.2382	0.3132	0.4591	0.7388	1.0071	1.3943
0.90	0.1630	0.1935	0.2383	0.3114	0.4527	0.7220	0.9793	1.3496
0.93	0.1664	0.1963	0.2405	0.3122	0.4507	0.7138	0.9648	1.3257
0.95	0.1705	0.1998	0.2432	0.3138	0.4501	0.7092	0.9561	1.3108
0.97	0.1779	0.2055	0.2474	0.3164	0.4504	0.7052	0.9480	1.2968
0.98	0.1844	0.2097	0.2503	0.3182	0.4508	0.7035	0.9442	1.2901
0.99	0.1959	0.2154	0.2538	0.3204	0.4514	0.7018	0.9406	1.2835
1.00	0.2901	0.2237	0.2583	0.3229	0.4522	0.7004	0.9372	1.2772
[illegible]	[illegible]	0.2370	0.2640	0.3260	0.4533	0.6991	0.9339	1.2710
[illegible]	[illegible]	0.2629	0.2715	0.3297	0.4547	0.6980	0.9307	1.2650
1.05	0.6026	0.4437	0.3131	0.3452	0.4604	0.6956	0.9222	1.2481
1.10	0.6880	0.5984	0.4580	0.3953	0.4770	0.6950	0.9110	1.2232
1.15	0.7443	0.6803	0.5798	0.4760	0.5042	0.6987	0.9033	1.2021
1.20	0.7858	0.7363	0.6605	0.5605	0.5425	0.7069	0.8990	1.1844
1.30	0.8438	0.8111	0.7624	0.6908	0.6344	0.7358	0.8998	1.1580
1.40	0.8827	0.8595	0.8256	0.7753	0.7202	0.7761	0.9112	1.1419
1.50	0.9103	0.8933	0.8689	0.8328	0.7887	0.8200	0.9297	1.1339
1.60	0.9308	0.9180	0.9000	0.8738	0.8410	0.8617	0.9518	1.1320
1.70	0.9463	0.9367	0.9234	0.9043	0.8809	0.8984	0.9745	1.1343
1.80	0.9583	0.9511	0.9413	0.9275	0.9118	0.9297	0.9961	1.1391
1.90	0.9678	0.9624	0.9552	0.9456	0.9359	0.9557	1.0157	1.1452
2.00	0.9754	0.9715	0.9664	0.9599	0.9550	0.9772	1.0328	1.1516
2.20	0.9856	0.9847	0.9826	0.9806	0.9827	1.0094	1.0600	1.1635
2.40	0.9941	0.9936	0.9935	0.9945	1.0011	1.0313	1.0793	1.1728
2.60	0.9993	0.9998	1.0010	1.0040	1.0137	1.0463	1.0926	1.1792
2.80	1.0031	1.0042	1.0063	1.0106	1.0223	1.0565	1.1016	1.1830
3.00	1.0057	1.0074	1.0101	1.0153	1.0284	1.0635	1.1075	1.1848
3.50	[illegible]	[illegible]	1.0156	1.0221	1.0368	1.0723	1.1138	1.1834
4.00	1.0115	1.0140	1.0179	1.0249	1.0401	1.0747	1.1136	1.1773

Table E.4: Values of Z^1

P_r = 1.731

P_r = / T_r	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
0.30	−0.0806	−0.0966	[illegible]	[illegible]	−0.2407	−0.3996	−0.5572	−0.7915
0.35	−0.0921	−0.1105	−0.1379	−0.1834	−0.2738	−0.4523	−0.6279	−0.8863
0.40	−0.0946	−0.1134	−0.1414	−0.1879	−0.2799	−0.4603	−0.6365	−0.8936
0.45	−0.0929	−0.1113	−0.1387	−0.1840	−0.2734	−0.4475	−0.6162	−0.8608
0.50	−0.0893	−0.1069	−0.1330	−0.1762	−0.2611	−0.4253	−0.5831	−0.8099
0.55	−0.0849	−0.1015	−0.1263	−0.1669	−0.2465	−0.3991	−0.5446	−0.7521
0.60	−0.0803	−0.0960	−0.1192	−0.1572	−0.2312	−0.3718	−0.5047	−0.6928
0.65	−0.0759	−0.0906	−0.1122	−0.1476	−0.2160	−0.3447	−0.4653	−0.6346
0.70	−0.0718	−0.0855	−0.1057	−0.1385	−0.2013	−0.3184	−0.4270	−0.5785
0.75	−0.0681	−0.0808	−0.0996	−0.1298	−0.1872	−0.2929	−0.3901	−0.5250
0.80	−0.0648	−0.0767	−0.0940	−0.1217	−0.1736	−0.2682	−0.3545	−0.4740
0.85	−0.0622	−0.0731	−0.0888	−0.1138	−0.1602	−0.2439	−0.3201	−0.4254
0.90	−0.0604	−0.0701	−0.0840	−0.1059	−0.1463	−0.2195	−0.2862	−0.3788
0.93	−0.0602	−0.0687	−0.0810	−0.1007	−0.1374	−0.2045	−0.2661	−0.3516
0.95	−0.0607	−0.0678	−0.0788	−0.0967	−0.1310	−0.1943	−0.2526	−0.3339
0.97	−0.0623	−0.0669	−0.0759	−0.0921	−0.1240	−0.1837	−0.2391	−0.3163
0.98	−0.0641	−0.0661	−0.0740	−0.0893	−0.1202	−0.1783	−0.2322	−0.3075
0.99	−0.0680	−0.0646	−0.0715	−0.0861	−0.1162	−0.1728	−0.2254	−0.2989
1.00	−0.0879	−0.0609	−0.0678	−0.0824	−0.1118	−0.1672	−0.2185	−0.2902
1.01	−0.0223	−0.0473	−0.0621	−0.0778	−0.1072	−0.1615	−0.2116	−0.2816
1.02	−0.0062	−0.0227	−0.0524	−0.0722	−0.1021	−0.1556	−0.2047	−0.2731
1.05	0.0220	0.1059	0.0451	−0.0432	−0.0838	−0.1370	−0.1835	−0.2476
1.10	0.0476	0.0897	0.1630	0.0698	−0.0373	−0.1021	−0.1469	−0.2056
1.15	0.0625	0.0943	0.1548	0.1667	0.0332	−0.0611	−0.1084	−0.1642
1.20	0.0719	0.0991	0.1477	0.1990	0.1095	−0.0141	−0.0678	−0.1231
1.30	0.0819	0.1048	0.1420	0.1991	0.2079	0.0875	0.0176	−0.0423
1.40	0.0857	0.1063	0.1383	0.1894	0.2397	0.1737	0.1008	0.0350
1.50	0.0854	0.1055	0.1345	0.1806	0.2433	0.2309	0.1717	0.1058
1.60	0.0855	0.1035	0.1303	0.1729	0.2381	0.2631	0.2255	0.1673
1.70	0.0838	0.1008	0.1259	0.1658	0.2305	0.2788	0.2628	0.2179
1.80	0.0816	0.0978	0.1216	0.1593	0.2224	0.2846	0.2871	0.2576
1.90	0.0792	0.0947	0.1173	0.1532	0.2144	0.2848	0.3017	0.2876
2.00	0.0767	0.0916	0.1133	0.1476	0.2069	0.2819	0.3097	0.3096
2.20	0.0719	0.0857	0.1057	0.1374	0.1932	0.2720	0.3135	0.3355
2.40	0.0675	0.0803	0.0989	0.1285	0.1812	0.2602	0.3089	0.3459
2.60	0.0634	0.0754	0.0929	0.1207	0.1706	0.2484	0.3009	0.3475
2.80	0.0598	0.0711	0.0876	0.1138	0.1613	0.2372	0.2915	0.3443
3.00	0.0535	0.0672	0.0828	0.1076	0.1529	0.2268	0.2817	0.3385
3.50	0.0497	0.0591	0.0728	0.0949	0.1356	0.2042	0.2584	0.3194
4.00	0.0443	0.0527	0.0651	0.0849	0.1219	0.1857	0.2378	0.2994

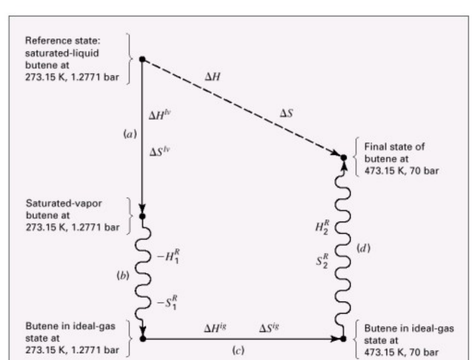


Figure 6.7: Calculational path for Ex. 6.9.

- Step (a): Vaporization of saturated liquid 1-butane at 0°C

$$\ln P^{sat} = A - \frac{B}{T} \quad \ldots(6.75)$$

- The vapor pressure curve contains both

$$\text{the normal boiling point;} \quad \ln 1.0133 = A - \frac{B}{266.9}$$

$$\text{the critical point;} \quad \ln 40.43 = A - \frac{B}{420.0}$$

$$\text{Whence,} \quad A = 10.126 \qquad B = 2{,}699.11$$

$$\boxed{\Delta H = T\,\Delta V \frac{dP^{sat}}{dT}} \quad (4.11) \qquad \frac{\Delta H_2}{\Delta H_1} = \left(\frac{1-T_{r_2}}{1-T_{r_1}}\right)^{0.38} \quad (4.13)$$

- The latent heat of vaporization, where T_{r_n}=266.9/420=0.635:

$$\frac{\Delta H_n^{lv}}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}} = \frac{1.092(\ln 40.43 - 1.013)}{0.930 - 0.636} = 9.979$$

$$\Delta H_n^{lv} = (9.979)(8.314)(266.9) = 22{,}137 \;\; Jmol^{-1}$$

5

- Step (b): Transformation of saturated vapor into an ideal gas at (T_1, P_1).

$$\frac{H^R}{RT_c} = P_r\left[B^0 - T_r\frac{dB^0}{dT_r} + \omega\left(B^1 - T_r\frac{dB^1}{dT_r}\right)\right] \ldots(6.87)$$

$$\frac{S^R}{R} = -P_r\left(\frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}\right) \quad \ldots(6.88)$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \ldots(3.65)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad \ldots(3.66)$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad \ldots(6.89)$$

$$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \quad \ldots(6.90)$$

- T_r = 0.650 and P_r = 1.2771/40.43 = 0.0316

$$So, \;\; H_1^R = (-0.0985)(8.314)(420) =$$

$$S_1^R = (-0.1063)(8.314) = -0.88 \;\; Jmol^{-1}K^{-1}$$

- Step (c): Changes in the ideal gas state

$$Eq.(6.95): \Delta H^{ig} = H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT = \langle C_P^{ig}\rangle_H (T_2 - T_1)$$

$$Eq.(6.96): \Delta S^{ig} = S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} C_P^{ig}\frac{dT}{T} - R\ln\frac{P_2}{P_1} = \langle C_P^{ig}\rangle_S \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

- T_{am} = 373.15 K, T_{lm} = 364.04 K, A = 1.967, B = 31.630x10^{-3}, C = -9.837x10^{-6}

ΔH^{ig} =

ΔS^{ig} = 22.18 J mol^{-1} K^{-1}

- Step (d): Transformation from the ideal gas to real gas state at T_2 and P_2.

  T_r = 1.127 P_r = 1.731 $\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega\frac{(H^R)^1}{RT_c} \ldots(6.85)$ $\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega\frac{(S^R)^1}{R} \ldots(6.86)$

- At the higher P; Eqs.( ) and ( ) with interpolated values from Table E.7, E.8, E.11 and E.12.

$$\frac{H_2^R}{RT_C} = -2.294 + (0.191)(-0.713) = -2.430$$

$$\frac{S_2^R}{R} = -1.566 + (0.191)(-0.726) = -1.705$$

$$\Rightarrow H_2^R = (-2.430)(8.314)(420.0) =$$

$$S_2^R = (-1.705)(8.314) = -14.18 \;\; Jmol^{-1}K^{-1}$$

Extension to Gas Mixtures

$$\omega \equiv \sum_i y_i\omega_i \ldots(6.97) \qquad T_{pc} \equiv \sum_i y_i T_{ci} \ldots(6.98) \qquad P_{pc} \equiv \sum_i y_i P_{ci} \ldots(6.99)$$

$$T_{Pr} = \frac{T}{T_{pc}} \quad \ldots(6.100) \qquad P_{Pr} = \frac{P}{P_{pc}} \quad \ldots(6.101)$$

These replace T_r and P_r for reading entries from the table of App. E, and lead to values of Z by Eq.(3.57), and H^R/RT_{pc} by Eq.(6.85), and S^R/R by Eq.(6.86).

Ex. 6.10

Estimate V, H^R, and S^R for an equimolar mixture of carbon dioxide(1) and propane(2) at 450 K and 140 bar by the Lee/Kesler correlations.

Solution

From Table B.1,

CO_2 propane

$$\omega = y_1\omega_1 + y_2\omega_2 = (0.5)(0.224) + (0.5)(0.152) = 0.188$$

$$T_{pc} = y_1T_{c1} + y_2T_{c2} = (0.5)(304.2) + (0.5)(369.8) = 337.0 \ K$$

$$P_{pc} = y_1P_{c1} + y_2P_{c2} = (0.5)(73.83) + (0.5)(42.48) = 58.15 \ bar$$

$$Whence, \ T_{pr} = \frac{450}{337.0} = 1.335 \qquad P_{pr} = \frac{140}{58.15} = 2.41$$

Table B.1: Characteristic Properties of Pure Species

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c cm^3 mol^{-1}	T_n/K
Methane	16.043	0.012	190.6	45.99	0.286	98.6	111.4
Ethane	30.070	0.100	305.3	48.72	0.279	145.5	184.6
Propane	44.097	0.152	369.8	42.48	0.276	200.0	231.1
n-Butane	58.123	0.200	425.1	37.96	0.274	255.	272.7
n-Pentane	72.150	0.252	469.7	33.70	0.270	313.	309.2
n-Hexane	86.177	0.301	507.6	30.25	0.266	371.	341.9
n-Heptane	100.204	0.350	540.2	27.40	0.261	428.	371.6
n-Octane	114.231	0.400	568.7	24.90	0.256	486.	398.8
n-Nonane	128.258	0.444	594.6	22.90	0.252	544.	424.0
n-Decane	142.285	0.492	617.7	21.10	0.247	600.	447.3
Isobutane	58.123	0.181	408.1	36.48	0.282	262.7	261.4
Isooctane	114.231	0.302	544.0	25.68	0.266	468.	372.4
Cyclopentane	70.134	0.196	511.8	45.02	0.273	258.	322.4
Cyclohexane	84.161	0.210	553.6	40.73	0.273	308.	353.9
Methylcyclopentane	84.161	0.230	532.8	37.85	0.272	319.	345.0
Methylcyclohexane	98.188	0.235	572.2	34.71	0.269	368.	374.1
Ethylene	28.054	0.087	282.3	50.40	0.281	131.	169.4
Propylene	42.081	0.140	365.6	46.65	0.289	188.4	225.5
1-Butene	56.108	0.191	420.0	40.43	0.277	239.3	266.9
cis-2-Butene	56.108	0.205	435.6	42.43	0.273	233.8	276.9
trans-2-Butene	56.108	0.218	428.6	41.00	0.275	237.7	274.0
1-Hexene	84.161	0.280	504.0	31.40	0.265	354.	336.3
Isobutylene	56.108	0.194	417.9	40.00	0.275	238.9	266.3
1,3-Butadiene	54.092	0.190	425.2	42.77	0.267	220.4	268.7
Cyclohexene	82.145	0.212	560.4	43.50	0.272	291.	356.1
Acetylene	26.038	0.187	308.3	61.39	0.271	113.	189.4
Benzene	78.114	0.210	562.2	48.98	0.271	259.	353.2
Toluene	92.141	0.262	591.8	41.06	0.264	316.	383.8
Ethylbenzene	106.167	0.303	617.2	36.06	0.263	374.	409.4
Cumene	120.194	0.326	631.1	32.09	0.261	427.	425.6
o-Xylene	106.167	0.310	630.3	37.34	0.263	369.	417.6
m-Xylene	106.167	0.326	617.1	35.36	0.259	376.	412.3
p-Xylene	106.167	0.322	616.2	35.11	0.260	379.	411.5
Styrene	104.152	0.297	636.0	38.40	0.256	352.	418.3
Naphthalene	128.174	0.302	748.4	40.51	0.269	413.	491.2
Biphenyl	154.211	0.365	789.3	38.50	0.295	502.	528.2
Formaldehyde	30.026	0.282	408.0	65.90	0.223	115.	254.1
Acetaldehyde	44.053	0.291	466.0	55.50	0.221	154.	294.0
Methyl acetate	74.079	0.331	506.6	47.50	0.257	228.	330.1
Ethyl acetate	88.106	0.366	523.3	38.80	0.255	286.	350.2
Acetone	58.080	0.307	508.2	47.01	0.233	209.	329.4
Methyl ethyl ketone	72.107	0.323	535.5	41.50	0.249	267.	352.8
Diethyl ether	74.123	0.281	466.7	36.40	0.263	280.	307.6
Methyl *t*-butyl ether	88.150	0.266	497.1	34.30	0.273	329.	328.4

Table B.1 (Continued)

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c cm^3 mol^{-1}	T_n/K
Methanol	32.042	0.564	512.6	80.97	0.224	118.	337.9
Ethanol	46.069	0.645	513.9	61.48	0.240	167.	351.4
1-Propanol	60.096	0.622	536.8	51.75	0.254	219.	370.4
1-Butanol	74.123	0.594	563.1	44.23	0.260	275.	390.8
1-Hexanol	102.177	0.579	611.4	35.10	0.263	381.	430.6
2-Propanol	60.096	0.668	508.3	47.62	0.248	220.	355.4
Phenol	94.113	0.444	694.3	61.30	0.243	229.	455.0
Ethylene glycol	62.068	0.487	719.7	77.00	0.246	191.0	470.5
Acetic acid	60.053	0.467	592.0	57.86	0.211	179.7	391.1
n-Butyric acid	88.106	0.681	615.7	40.64	0.232	291.7	436.4
Benzoic acid	122.123	0.603	751.0	44.70	0.246	344.	522.4
Acetonitrile	41.053	0.338	545.5	48.30	0.184	173.	354.8
Methylamine	31.057	0.281	430.1	74.60	0.321	154.	266.8
Ethylamine	45.084	0.285	456.2	56.20	0.307	207.	289.7
Nitromethane	61.040	0.348	588.2	63.10	0.223	173.	374.4
Carbon tetrachloride	153.822	0.193	556.4	45.60	0.272	276.	349.8
Chloroform	119.377	0.222	536.4	54.72	0.293	239.	334.3
Dichloromethane	84.932	0.199	510.0	60.80	0.265	185.	312.9
Methyl chloride	50.488	0.153	416.3	66.80	0.276	143.	249.1
Ethyl chloride	64.514	0.190	460.4	52.70	0.275	200.	285.4
Chlorobenzene	112.558	0.250	632.4	45.20	0.265	308.	404.9
Tetrafluoroethane	102.030	0.327	374.2	40.60	0.258	198.0	247.1
Argon	39.948	0.000	150.9	48.98	0.291	74.6	87.3
Krypton	83.800	0.000	209.4	55.02	0.288	91.2	119.8
Xenon	131.30	0.000	289.7	58.40	0.286	118.0	165.0
Helium 4	4.003	−0.390	5.2	2.28	0.302	57.3	4.2
Hydrogen	2.016	−0.216	33.19	13.13	0.305	64.1	20.4
Oxygen	31.999	0.022	154.6	50.43	0.288	73.4	90.2
Nitrogen	28.014	0.038	126.2	34.00	0.289	89.2	77.3
Air†	28.851	0.035	132.2	37.45	0.289	84.8	
Chlorine	70.905	0.069	417.2	77.10	0.265	124.	239.1
Carbon monoxide	28.010	0.048	132.9	34.99	0.299	93.4	81.7
Carbon dioxide	44.010	0.224	304.2	73.83	0.274	94.0	
Carbon disulfide	76.143	0.111	552.0	79.00	0.275	160.	319.4
Hydrogen sulfide	34.082	0.094	373.5	89.63	0.284	98.5	212.8
Sulfur dioxide	64.065	0.245	430.8	78.84	0.269	122.	263.1
Sulfur trioxide	80.064	0.424	490.9	82.10	0.255	127.	317.9
Nitric oxide (NO)	30.006	0.583	180.2	64.80	0.251	58.0	121.4
Nitrous oxide (N_2O)	44.013	0.141	309.6	72.45	0.274	97.4	184.7
Hydrogen chloride	36.461	0.132	324.7	83.10	0.249	81.	188.2
Hydrogen cyanide	27.026	0.410	456.7	53.90	0.197	139.	298.9
Water	18.015	0.345	647.1	220.55	0.229	55.9	373.2
Ammonia	17.031	0.253	405.7	112.80	0.242	72.5	239.7
Nitric acid	63.013	0.714	520.0	68.90	0.231	145.	356.2
Sulfuric acid	98.080	...	924.0	64.00	0.147	177.	610.0

†Pseudoparameters for $y_{N_2} = 0.79$ and $y_{O_2} = 0.21$. See Eqs. (6.97)-(6.99).

$$From \ Table \ E.3 \ and \ E.4;$$

$$Z = Z^0 + \omega Z^1 = 0.697 + (0.188)(0.205) = 0.736$$

$$\Rightarrow V = \frac{ZRT}{P} = \frac{(0.736)(83.14)(450)}{140} = 196.7 \ cm^3 mol^{-1}$$

$$From \ Table \ E.7 \ and \ E.8; \ with \ Eq.(6.85):$$

$$\left(\frac{H^R}{RT_{pc}}\right)^0 = -1.730 \qquad \left(\frac{H^R}{RT_{pc}}\right)^1 = -0.169$$

$$\frac{H^R}{RT_{pc}} = -1.730 + (0.188)(-0.169) = -1.762$$

$$H^R = (8.314)(337)(-1.762) = -4{,}937 \ Jmol^{-1}$$

$$From \ Table \ E.11 \ and \ E.12; \ with \ Eq.(6.86):$$

$$\frac{S^R}{R} = -0.967 + (0.188)(-0.330) = -1.029$$

$$S^R = (8.314)(-1.029) = -8.56 Jmol^{-1}K^{-1}$$

End of Part 3

1st year En23KKU 1986