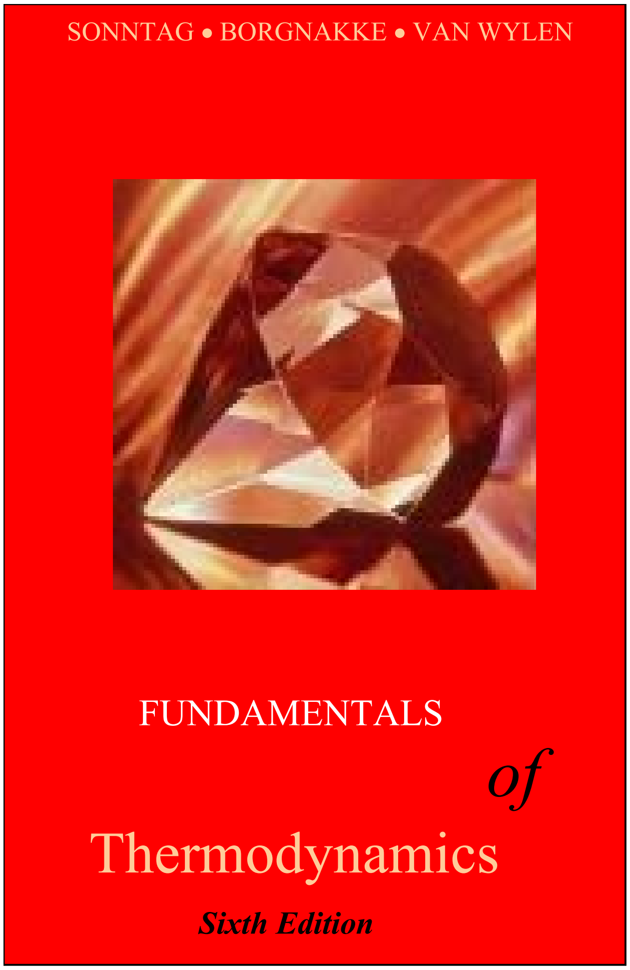
CHAPTER 13
SOLUTION MANUAL



Fundamentals of Thermodynamics 6th Edition
Sonntag, Borgnakke and van Wylen

CONTENT CHAPTER 13

CHAPTER 13 6th ed. CORRESPONDANCE TABLE

The new problem set relative to the problems in the fifth edition.

New	5th	New	5th	New	5th	New	5th
		50	new	80	50	110	46
21	1	51	new	81	33	111	55
22	3	52	new	82	34	112	57
23	new	53	new	83	35	113	62
24	2	54	new	84	39	114	65
25	4	55	22	85	42	115	69
26	new	56	25	86	56	116	70
27	new	57	24a	87	44	117	67
28	new	58	24b	88	45	118	74a
29	6	59	47b	89	48	119	74b
30	7	60	29	90	51		
31	5	61	23	91	52		
32	9	62	27a	92	53		
33	8	63	27b	93	58a		
34	new	64	28	94	58b		
35	11	65	30	95	new		
36	new	66	68	96	new		
37	10	67	new	97	new		
38	12	68	new	98	54		
39	new	69	20	99	new		
40	new	70	21	100	new		
41	13	71	31	101	new		
42	new	72	38	102	60		
43	16	73	new	103	37		
44	new	74	new	104	61		
45	17	75	36	105	73a,b		
46	new	76	43	106	73a,c		
47	14	77	47a	107	26		
48	new	78	new	108	40		
49	15	79	49	109	41		

The English-unit problems are:

New	**5th**	**SI**	**New**	**5th**	**SI**	**New**	**5th**	**SI**
120	75	21mod	130	83	69	140	97	86
121	76	22	131	84	70	141	93	90
122	new	27	132	82	73	142	96	92
123	77	31	133	86	74	143	new	95
124	78	41	134	95	75	144	90	108
125	81	45	135	92	76	145	89	109
126	79	47	136	87	81			
127	80	49	137	88	82			
128	new	51	138	94	80			
129	85	65	139	91	85			

mod indicates a modification from the previous problem that changes the solution but otherwise is the same type problem.

The following table gives the values for the compressibility, enthalpy departure and the entropy departure along the saturated liquid-vapor boundary. These are used for all the problems using generalized charts as the figures are very difficult to read accurately (consistently) along the saturated liquid line. It is suggested that the instructor hands out copies of this page or let the students use the computer for homework solutions.

T_r	P_r	Z_f	Z_g	$d(h/RT)_f$	$d(h/RT)_g$	$d(s/R)_f$	$d(s/R)_g$
0.96	0.78	0.14	0.54	3.65	1.39	3.45	1.10
0.94	0.69	0.12	0.59	3.81	1.19	3.74	0.94
0.92	0.61	0.10	0.64	3.95	1.03	4.00	0.82
0.90	0.53	0.09	0.67	4.07	0.90	4.25	0.72
0.88	0.46	0.08	0.70	4.17	0.78	4.49	0.64
0.86	0.40	0.07	0.73	4.26	0.69	4.73	0.57
0.84	0.35	0.06	0.76	4.35	0.60	4.97	0.50
0.82	0.30	0.05	0.79	4.43	0.52	5.22	0.45
0.80	0.25	0.04	0.81	4.51	0.46	5.46	0.39
0.78	0.21	0.035	0.83	4.58	0.40	5.72	0.35
0.76	0.18	0.03	0.85	4.65	0.34	5.98	0.31
0.74	0.15	0.025	0.87	4.72	0.29	6.26	0.27
0.72	0.12	0.02	0.88	4.79	0.25	6.54	0.23
0.70	0.10	0.017	0.90	4.85	0.21	6.83	0.20
0.68	0.08	0.014	0.91	4.92	0.18	7.14	0.17
0.66	0.06	0.01	0.92	4.98	0.15	7.47	0.15
0.64	0.05	0.009	0.94	5.04	0.12	7.81	0.12
0.60	0.03	0.005	0.95	5.16	0.08	8.56	0.08
0.58	0.02	0.004	0.96	5.22	0.06	8.97	0.07
0.54	0.01	0.002	0.98	5.34	0.03	9.87	0.04
0.52	0.0007	0.0014	0.98	5.41	0.02	10.38	0.03

Concept-Study Guide Problems

13.1

Mention two uses of the Clapeyron equation.

If you have experimental information about saturation properties down to a certain temperature Clapeyron equation will allow you to make an intelligent curve extrapolation of the saturated pressure versus temperature function Psat(T) for lower temperatures.

From Clapeyrons equation we can calculate a heat of evaporation, heat of sublimation or heat of fusion based on measurable properties P, T and v.

13.2

The slope dP/dT of the vaporization line is finite as you approach the critical point, yet h_{fg} and v_{fg} both approach zero. How can that be?

The slope is $dP/dT = h_{fg} / Tv_{fg}$

Recall the math problem what is the limit of f(x)/g(x) when x goes towards a point where both functions f and g goes towards zero. A finite limit for the ratio is obtained if both first derivatives are different from zero so we have

$$dP/dT \rightarrow [dh_{fg} /dT] / d(Tv_{fg})/dT \quad \text{as} \quad T \rightarrow T_c$$

13.3

In view of Clapeyron's equation and Fig. 3.7, is there something special about ice I versus the other forms of ice?

Yes. The slope of the phase boundary dP/dT is negative for ice I to liquid whereas it is positive for all the other ice to liquid interphases. This also means that these other forms of ice are all heavier than liquid water. The pressure must be more than 200 MPa = 2000 atm so even the deepest ocean cannot reach that pressure (recall about 1 atm per 10 meters down).

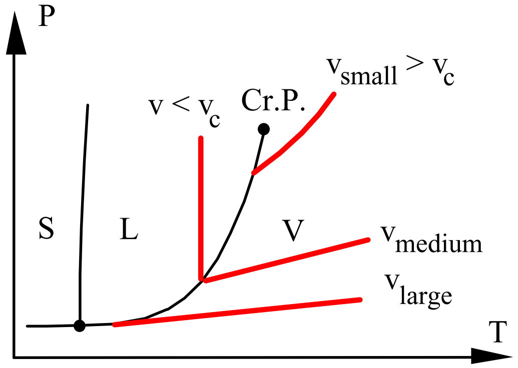
13.4

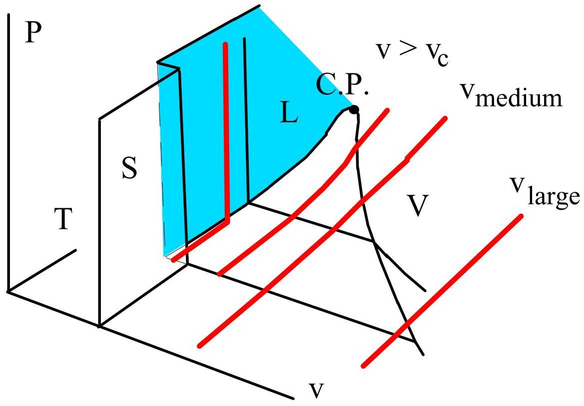
If we take a derivative as $(\partial P/\partial T)_v$ in the two-phase region, see Figs. 3.18 and 3.19, does it matter what v is? How about T?

In the two-phase region, P is a function only of T, and not dependent on v.

13.5

Sketch on a P-T diagram how a constant v line behaves in the compressed liquid region, the two-phase L-V region and the superheated vapor region?





13.6

If I raise the pressure in an isentropic process, does h go up or down? Is that independent upon the phase?

$T ds = 0 = dh - v dP$, so h increases as P increases, for any phase. The magnitude is proportional to v (i.e. large for vapor and small for liquid and solid phases)

13.7

If I raise the pressure in an isothermal process does h go up or down for a liquid or solid? What do you need to know if it is a gas phase?

Eq. 13.25: $\left(\frac{\partial h}{\partial P}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_P = v[1 - T\alpha_P]$

Liquid or solid, α_P is very small, h increases with P ;

For a gas, we need to know the equation of state.

13.8

The equation of state in Example 13.3 was used as explicit in v. Is it explicit in P?

Yes, the equation can be written explicitly in P.

$$P = RT / [v + C/T^3]$$

13.9

Over what range of states are the various coefficients in Section 13.5 most useful?

For solids or liquids, where the coefficients are essentially constant over a wide range of P's and T's.

13.10

For a liquid or a solid is v more sensitive to T or P? How about an ideal gas?

For a liquid or solid, v is more sensitive to T than P.

For an ideal gas, $v = RT/P$, varies directly with T, inversely with P.

13.11

If I raise the pressure in a solid at constant T, does s go up or down?

In Example 13.4, it is found that change in s with P at constant T is negatively related to volume expansivity (a positive value for a solid), $ds_T = - v\ \alpha_P\ dP_T$, so raising P decreases s.

13.12

Most equations of state are developed to cover which range of states?

Most equations of state are developed to cover the gaseous phase, from low to moderate densities. Many cover high-density regions as well, including the compressed liquid region.

13.13

Is an equation of state valid in the two-phase regions?

No. In a two-phase region, P depends only on T. There is a discontinuity at each phase boundary.

13.14

As $P \rightarrow 0$, the specific volume $v \rightarrow \infty$. For $P \rightarrow \infty$, does $v \rightarrow 0$?

At very low P, the substance will be essentially an ideal gas, $Pv = RT$, so that v becomes very large. However at very high P, the substance eventually must become a solid, which cannot be compressed to a volume approaching zero.

13.15

Must an equation of state satisfy the two conditions in Eqs. 13.50 and 13.51?

It has been observed from experimental measurements that substances do behave in that manner. If an equation of state is to be accurate in the near-critical region, it would have to satisfy these two conditions.

If the equation is simple it may be overly restrictive to inpose these as it may lead to larger inaccuracies in other regions.

13.16

At which states are the departure terms for h and s small? What is Z there?

Departure terms for h and s are small at very low pressure or at very high temperature. In both cases, Z is close to 1.

13.17

What is the benefit of the generalized charts? Which properties must be known besides the charts themselves?

The generalized charts allow for the approximate calculations of enthalpy and entropy changes (and P,v,T behavior), for processes in cases where specific data or equation of state are not known. They also allow for approximate phase boundary determinations. It is necessary to know the critical pressure and temperature, as well as ideal-gas specific heat.

13.18

What does it imply if the compressibility factor is larger than 1?

Compressibility factor greater than one results from domination of intermolecular forces of repulsion (short range) over forces of attraction (long range) – either high temperature or very high density. This implies that the density is lower than what is predicted by the ideal gas law, the ideal gas law assumes the molecules (atoms) can be pressed closer together.

13.19

The departure functions for h and s as defined are always positive. What does that imply for the real substance h and s values relative to ideal gas values?

Real-substance h and s are less than the corresponding ideal-gas values.

13.20

What is the benefit of Kay’s rule versus a mixture equation of state?

Kay’s rule for a mixture is not nearly as accurate as an equation of state for the mixture, but it is very simple to use.

Clapeyron Equation

13.21

A special application requires R-12 at −140°C. It is known that the triple-point temperature is −157°C. Find the pressure and specific volume of the saturated vapor at the required condition.

The lowest temperature in Table B.3 for R-12 is -90°C, so it must be extended to -140°C using the Clapeyron Eq. 13.7 integrated as in example 13.1

Table B.3: at $T_1 = -90^{o}C = 183.2$ K, $P_1 = 2.8$ kPa.

$$R = \frac{8.3145}{120.914} = 0.068\ 76 \text{ kJ/kg K}$$

$$\ln\frac{P}{P_1} = \frac{h_{fg}}{R}\ \frac{(T - T_1)}{T \times T_1} = \frac{189.748}{0.068\ 76}\ \frac{(133.2 - 183.2)}{133.2 \times 183.2} = -5.6543$$

$P = 2.8 \exp(-5.6543) =$ **0.0098 kPa**

13.22

Ice (solid water) at –3°C, 100 kPa, is compressed isothermally until it becomes liquid. Find the required pressure.

Water, triple point $T = 0.01^{o}C$, $P = 0.6113$ kPa

Table B.1.1: $v_f = 0.001\ m^3/kg$, $h_f = 0.01$ kJ/kg,

Tabel B.1.5: $v_i = 0.001\ 0908\ m^3/kg$, $h_i = -333.4$ kJ/kg

Clapeyron $$\frac{dP_{if}}{dT} = \frac{h_f - h_i}{(v_f - v_i)T} = \frac{333.4}{-0.0000908 \times 273.16} = -13\ 442 \text{ kPa/K}$$

$$\Delta P \approx \frac{dP_{if}}{dT} \Delta T = -13\ 442(-3 - 0.01) = 40\ 460 \text{ kPa}$$

$$P = P_{tp} + \Delta P = \mathbf{40\ 461\ kPa}$$

13.23

An approximation for the saturation pressure can be ln $P_{sat} = A - B/T$, where A and B are constants. Which phase transition is that suitable for, and what kind of property variations are assumed?

Clapeyron Equation expressed for the three phase transitions are shown in Eqs. 13.5-13.7. The last two leads to a natural log function if integrated and ideal gas for the vapor is assumed.

$$\frac{dP_{sat}}{dT} = P_{sat} \frac{h_{evap}}{RT^2}$$

where h_{evap} is either h_{fg} or h_{ig}. Separate the variables and integrate

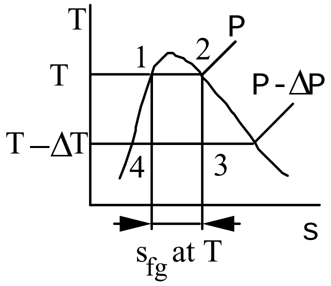
$$P_{sat}^{-1}\, dP_{sat} = h_{evap}\, R^{-1}\, T^{-2}\, dT$$

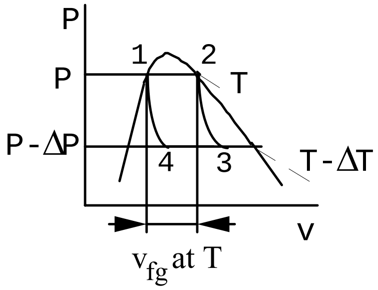
$$\ln P_{sat} = A - B/T\,; \qquad B = h_{evap}\, R^{-1}$$

if we also assume h_{evap} is constant and A is an integration constant. The function then applies to the liquid-vapor and the solid-vapor interphases with different values of A and B. As h_{evap} is not excactly constant over a wide interval in T means that the equation cannot be used for the total domain.

13.24

In a Carnot heat engine, the heat addition changes the working fluid from saturated liquid to saturated vapor at *T*, *P*. The heat rejection process occurs at lower temperature and pressure $(T - \Delta T)$, $(P - \Delta P)$. The cycle takes place in a piston cylinder arrangement where the work is boundary work. Apply both the first and second law with simple approximations for the integral equal to work. Then show that the relation between ΔP and ΔT results in the Clapeyron equation in the limit $\Delta T \rightarrow dT$.





$$q_H = Ts_{fg}; \quad q_L = (T\text{-}\Delta T)s_{fg} \;; \qquad w_{net} = q_H - q_L = \Delta T s_{fg}$$

Problem similar to development in section 13.1 for shaft work, here boundary movement work, $w = \int P dv$

$$w_{NET} = P(v_2\text{-}v_1) + \int_2^3 Pdv + (P - \Delta P)(v_4 - v_3) + \int_1^4 Pdv$$

Approximating,

$$\int_2^3 Pdv \approx \left(P - \frac{\Delta P}{2}\right)\left(v_3 - v_2\right); \qquad \int_1^4 Pdv \approx \left(P - \frac{\Delta P}{2}\right)\left(v_1 - v_4\right)$$

Collecting terms: $\quad w_{NET} \approx \Delta P\left[\left(\frac{v_2+v_3}{2}\right) - \left(\frac{v_1+v_4}{2}\right)\right]$

(the smaller the ΔP, the better the approximation)

$$\Rightarrow \frac{\Delta P}{\Delta T} \approx \frac{s_{fg}}{\frac{1}{2}(v_2 + v_3) - \frac{1}{2}(v_1 + v_4)}$$

In the limit as $\quad \Delta T \rightarrow 0: \quad v_3 \rightarrow v_2 = v_g , \quad v_4 \rightarrow v_1 = v_f$

$$\& \lim_{\Delta T \rightarrow 0} \frac{\Delta P}{\Delta T} = \frac{dP_{sat}}{dT} = \frac{s_{fg}}{v_{fg}}$$

13.25

Calculate the values h_{fg} and s_{fg} for nitrogen at 70 K and at 110 K from the Clapeyron equation, using the necessary pressure and specific volume values from Table B.6.1.

Clapeyron equation Eq.13.7: $\frac{dP_g}{dT} = \frac{h_{fg}}{Tv_{fg}} = \frac{s_{fg}}{v_{fg}}$

For N_2 at 70 K, using values for P_g from Table B.6 at 75 K and 65 K, and also v_{fg} at 70 K,

$$h_{fg} \approx T(v_g\text{-}v_f)\frac{\Delta P_g}{\Delta T} = 70(0.525\ 015)\left(\frac{76.1\text{-}17.41}{75\text{-}65}\right) = 215.7 \text{ kJ/kg} \ \ (207.8)$$

$$s_{fg} = h_{fg}/T = 3.081 \text{ kJ/kg K} \ \ (2.97)$$

Comparison not very close because P_g not linear function of T. Using 71 K & 69 K from the software,

$$h_{fg} = 70(0.525\ 015)\left(\frac{44.56\text{-}33.24}{71\text{-}69}\right) = 208.0 \text{ kJ/kg}$$

At 110 K, $h_{fg} \approx 110(0.014\ 342)\left(\frac{1938.8\text{-}1084.2}{115\text{-}105}\right) = 134.82 \text{ kJ/kg} \ \ (134.17)$

$$s_{fg} = \frac{134.82}{110} = 1.226 \text{ kJ/kg K} \ \ (1.22)$$

13.26

Ammonia at –70°C is used in a special application at a quality of 50%. Assume the only table available is B.2 that goes down to –50°C. To size a tank to hold 0.5 kg with x = 0.5, give your best estimate for the saturated pressure and the tank volume.

To size the tank we need the volume and thus the specific volume. If we do not have the table values for v_f and v_g we must estimate those at the lower T. We therefore use Clapeyron equation to extrapolate from –50°C to –70°C to get the saturation pressure and thus v_g assuming ideal gas for the vapor.

The values for v_f and h_{fg} do not change significantly so we estimate
Between -50°C and –70°C: $v_f = 0.001375\ \mathrm{m^3/kg}$, $h_{fg} = 1430\ \mathrm{kJ/kg}$

The integration of Eq.13.7 is the same as in Example 13.1 so we get

$$\ln\frac{P_2}{P_1} = \frac{h_{fg}}{R}\left(\frac{T_2 - T_1}{T_2T_1}\right) = \frac{1430}{0.4882}\,\frac{-70 + 50}{203.15 \times 223.15} = -1.2923$$

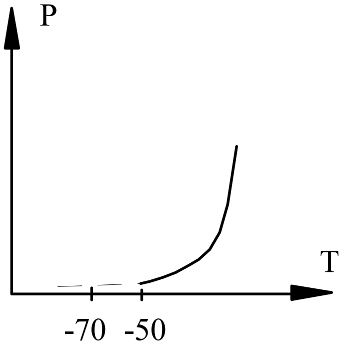
$$P_2 = P_1 \exp(-1.2923) = 40.9 \exp(-1.2923) = 11.2\ \mathrm{kPa}$$

$$v_g = RT_2/P_2 = \frac{0.4882 \times 203.15}{11.2} = 8.855\ \mathrm{m^3/kg}$$

$$v_2 = (1\text{-}x)\, v_f + x\, v_g = 0.5 \times 0.001375 + 0.5 \times 8.855 = 4.428\ \mathrm{m^3/kg}$$

$$V_2 = mv_2 = \mathbf{2.214\ m^3}$$

A straight line extrapolation will give a negative pressure.



13.27

The saturation pressure can be approximated as $\ln P_{sat} = A - B/T$, where A and B are constants. Use the steam tables and determine A and B from properties at 25^o C only. Use the equation to predict the saturation pressure at 30^oC and compare to table value.

$$\ln P_{sat} = A - B/T \qquad \Rightarrow \qquad \frac{dP_{sat}}{dT} = P_{sat}\,(-B)(-T^{-2})$$

so we notice from Eq.13.7 and Table values from B.1.1 and A.5 that

$$B = \frac{h_{fg}}{R} = \frac{2442.3}{0.4615} = 5292 \text{ K}$$

Now the constant A comes from the saturation pressure as

$$A = \ln P_{sat} + B/T = \ln 3.169 + \frac{5292}{273.15 + 25} = 18.9032$$

Use the equation to predict the saturation pressure at 30C as

$$\ln P_{sat} = A - B/T = 18.9032 - \frac{5292}{273.15 + 30} = 1.4462$$

$$P_{sat} = 4.2469 \text{ kPa}$$

compare this with the table value of $P_{sat} = 4.246$ kPa and we have a very close approximation.

13.28

Using the properties of water at the triple point, develop an equation for the saturation pressure along the fusion line as a function of temperature.

Solution:

The fusion line is shown in Fig. 3.4 as the S-L interphase. From Eq.13.5 we have

$$\frac{dP_{fusion}}{dT} = \frac{h_{if}}{Tv_{if}}$$

Assume h_{if} and v_{if} are constant over a range of T's. We do not have any simple models for these as function of T other than curve fitting. Then we can integrate the above equation from the triple point (T_1, P_1) to get the pressure P(T) as

$$P - P_1 = \frac{h_{if}}{v_{if}} \ln \frac{T}{T_1}$$

Now take the properties at the triple point from B.1.1 and B.1.5

$$P_1 = 0.6113 \text{ kPa}, \quad T_1 = 273.16 \text{ K}$$

$$v_{if} = v_f - v_i = 0.001 - 0.0010908 = -9.08 \times 10^{-5} \text{ m}^3\text{/kg}$$

$$h_{if} = h_f - h_i = 0.0 - (-333.4) = 333.4 \text{ kJ/kg}$$

The function that approximates the pressure becomes

$$P = 0.6113 - 3.672 \times 10^6 \ln \frac{T}{T_1} \quad [\text{kPa}]$$

13.29

Helium boils at 4.22 K at atmospheric pressure, 101.3 kPa, with h_{fg} = 83.3 kJ/kmol. By pumping a vacuum over liquid helium, the pressure can be lowered, and it may then boil at a lower temperature. Estimate the necessary pressure to produce a boiling temperature of 1 K and one of 0.5 K.

Solution:

Helium at 4.22 K: P_1 = 0.1013 MPa, $\bar{h}_{FG}$ = 83.3 kJ/kmol

$$\frac{dP_{SAT}}{dT} = \frac{h_{FG}}{Tv_{FG}} \approx \frac{h_{FG}P_{SAT}}{RT^2} \quad \Rightarrow \quad \ln\frac{P_2}{P_1} = \frac{h_{FG}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

For T_2 = 1.0 K:

$$\ln\frac{P_2}{101.3} = \frac{83.3}{8.3145}\left[\frac{1}{4.22} - \frac{1}{1.0}\right] \quad => \quad P_2 = 0.048 \text{ kPa} = \mathbf{48\ Pa}$$

For T_2 = 0.5 K:

$$\ln\frac{P_2}{101.3} = \frac{83.3}{8.3145}\left[\frac{1}{4.22} - \frac{1}{0.5}\right]$$

$P_2 = 2.1601\times10^{-6}$ kPa = $\mathbf{2.1601 \times 10^{-3}}$ **Pa**

13.30

A certain refrigerant vapor enters a steady flow constant pressure condenser at 150 kPa, 70°C, at a rate of 1.5 kg/s, and it exits as saturated liquid. Calculate the rate of heat transfer from the condenser. It may be assumed that the vapor is an ideal gas, and also that at saturation, $v_f << v_g$. The following quantities are known for this refrigerant:

$$\ln P_g = 8.15 - 1000/T\,; \qquad C_P = 0.7 \text{ kJ/kg K}$$

with pressure in kPa and temperature in K. The molecular weight is 100.

Refrigerant: State 1 $T_1 = 70^oC$ $P_1 = 150$ kPa

State 2 $P_2 = 150$ kPa $x_2 = 1.0$ State 3 $P_3 = 150$ kPa $x_3 = 0.0$

Get the saturation temperature at the given pressure

$$\ln (150) = 8.15 - 1000/T_2 \;\Rightarrow\; T_2 = 318.5 \text{ K} = 45.3^oC = T_3$$

$$_1q_3 = h_3 - h_1 = (h_3 - h_2) + (h_2 - h_1) = - h_{fg\,T3} + C_{P0}(T_2 - T_1)$$

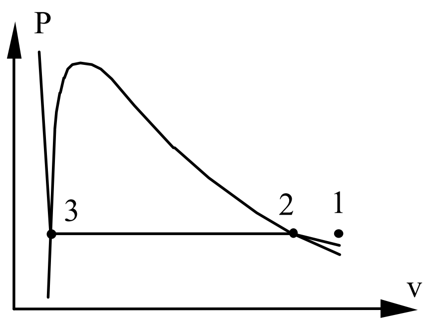
$$\frac{dP_g}{dT} = \frac{h_{fg}}{Tv_{fg}}, \qquad v_{fg} \approx v_g = \frac{RT}{P_g}, \qquad \frac{dP_g}{dT} = P_g\frac{d\ln P_g}{dT} = \frac{h_{fg}}{RT^2}P_g$$

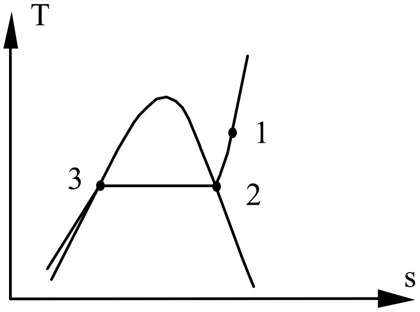
$$\frac{d\ln P_g}{dT} = +1000/T^2 = h_{fg}/RT^2$$

$$h_{fg} = 1000 \times R = 1000 \times 8.3145/100 = 83.15 \text{ kJ/kg}$$

$$_1q_3 = -83.15 + 0.7(45.3 - 70) = -100.44 \text{ kJ/kg}$$

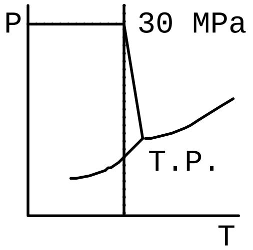
$$\dot{Q}_{COND} = 1.5(-100.44) = \mathbf{-150.6\ kW}$$





13.31

Using thermodynamic data for water from Tables B.1.1 and B.1.5, estimate the freezing temperature of liquid water at a pressure of 30 MPa.



$$H_2O \quad \frac{dP_{if}}{dT} = \frac{h_{if}}{Tv_{if}} \approx \text{const}$$

At the triple point,

$$v_{if} = v_f - v_i = 0.001\ 000 - 0.001\ 090\ 8 = -0.000\ 090\ 8\ \text{m}^3/\text{kg}$$

$$h_{if} = h_f - h_i = 0.01 - (-333.40) = 333.41\ \text{kJ/kg}$$

$$\frac{dP_{if}}{dT} = \frac{333.41}{273.16(-0.000\ 090\ 8)} = -13\ 442\ \text{kPa/K}$$

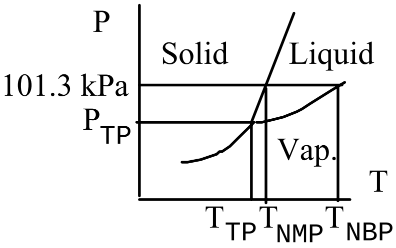
$\Rightarrow$ at P = 30 MPa,

$$T \approx 0.01 + \frac{(30\ 000-0.6)}{(-13\ 442)} = \mathbf{-2.2\ ^oC}$$

13.32

Small solid particles formed in combustion should be investigated. We would like to know the sublimation pressure as a function of temperature. The only information available is *T*, h_{FG} for boiling at 101.3 kPa and *T*, h_{IF} for melting at 101.3 kPa. Develop a procedure that will allow a determination of the sublimation pressure, $P_{sat}(T)$.

T_{NBP} = normal boiling pt T.
T_{NMP} = normal melting pt T.
T_{TP} = triple point T.



1) $T_{TP} \approx T_{NMP}$

2) $$\int_{0.1013\text{ MPa}}^{P_{TP}} (1/P_{SAT})\, dP_{SAT} \approx \int_{T_{NMP}}^{T_{TP}} \frac{h_{FG}}{RT^2}\, dT$$

Since $h_{FG} \approx \text{const} \approx h_{FG\,NBP}$ the integral over temperature becomes

$$\ln \frac{P_{TP}}{0.1013} \approx \frac{h_{FG\,NBP}}{R}\left[\frac{1}{T_{NBP}} - \frac{1}{T_{TP}}\right] \quad \rightarrow \quad \text{get } P_{TP}$$

3) $h_{IG\text{ at }TP} = h_G - h_I = (h_G - h_F) + (h_F - h_I) \approx h_{FG\,NBP} + h_{IF\,NMP}$

Assume $h_{IG} \approx$ const. again we can evaluate the integral

$$\ln \frac{P_{SUB}}{P_{TP}} = \int_{P_{TP}}^{P_{SUB}} (1/P_{SUB})\, dP_{SUB} \approx \int_{T_{TP}}^{T} \frac{h_{IG}}{RT^2}\, dT \approx \frac{h_{IG}}{R}\left[\frac{1}{T_{TP}} - \frac{1}{T}\right]$$

or $P_{SUB} = \text{fn}(T)$

13.33

A container has a double wall where the wall cavity is filled with carbon dioxide at room temperature and pressure. When the container is filled with a cryogenic liquid at 100 K the carbon dioxide will freeze so that the wall cavity has a mixture of solid and vapor carbon dioxide at the sublimation pressure. Assume that we do not have data for CO_2 at 100 K, but it is known that at −90°C: $P_{sat} = 38.1$ kPa, $h_{IG} = 574.5$ kJ/kg. Estimate the pressure in the wall cavity at 100 K.

Solution:

For CO_2 space: at $T_1 = -90\ ^oC = 183.2$ K , $P_1 = 38.1$ kPa, $h_{IG} = 574.5$ kJ/kg

For $T_2 = T_{CO2} = 100$ K: Clapeyron $\frac{dP_{SUB}}{dT} = \frac{h_{IG}}{Tv_{IG}} \approx \frac{h_{IG}P_{SUB}}{RT^2}$

$$\ln\frac{P_2}{P_1} = \frac{h_{IG}}{R}\left[\frac{1}{183.2} - \frac{1}{100}\right] = \frac{574.5}{0.188\,92}\left[\frac{1}{183.2} - \frac{1}{100}\right] = -13.81$$

or $P_2 = P_1 \times 1.005\times10^{-6} \Rightarrow P_2 = 3.83\times10^{-5}$ kPa = $\mathbf{3.83\times10^{-2}}$ **Pa**

Property Relations

13.34

Use Gibbs relation du = Tds – Pdv and one of Maxwell's relations to find an expression for $(\partial u/\partial P)_T$ that only has properties P, v and T involved. What is the value of that partial derivative if you have an ideal gas?

du = Tds – Pdv divide this by dP so we get

$$\left(\frac{\partial u}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T$$

where we have used Maxwell Eq.13.23. Now for an ideal gas we get

Ideal gas: $Pv = RT \quad \Rightarrow \quad v = \frac{RT}{P}$

then the derivatives are

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} \quad \text{and} \quad \left(\frac{\partial v}{\partial P}\right)_T = -RTP^{-2}$$

and the derivative of u is

$$\left(\frac{\partial u}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T = -T\frac{R}{P} - P(-RTP^{-2}) = 0$$

This confirm that u is not sensitive to P and only a function of T.

13.35

Start from Gibbs relation dh = Tds + vdP and use one of Maxwell's equation to get $(\partial h/\partial v)_T$ in terms of properties P, v and T. Then use Eq.13.24 to also find an expression for $(\partial h/\partial T)_v$.

Find $\left(\frac{\partial h}{\partial v}\right)_T$ and $\left(\frac{\partial h}{\partial T}\right)_v$

dh = Tds + vdP and use Eq.13.22

$$\Rightarrow \quad \left(\frac{\partial h}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T + v\left(\frac{\partial P}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T$$

Also for the second first derivative use Eq.13.28

$$\left(\frac{\partial h}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial T}\right)_v = C_v + v\left(\frac{\partial P}{\partial T}\right)_v$$

13.36

From Eqs. 13.23 and 13.24 and the knowledge that $C_p > C_v$ what can you conclude about the slopes of constant v and constant P curves in a T-s diagram? Notice that we are looking at functions T(s, P or v given).

Solution:

The functions and their slopes are:

Constant v: T(s) at that v with slope $\left(\frac{\partial T}{\partial s}\right)_v$

Constant P: T(s) at that P with slope $\left(\frac{\partial T}{\partial s}\right)_P$

Slopes of these functions are now evaluated using Eq.13.23 and Eq.13.24 as

$$\left(\frac{\partial T}{\partial s}\right)_P = \left(\left(\frac{\partial s}{\partial T}\right)_P\right)^{-1} = \frac{T}{C_p}$$

$$\left(\frac{\partial T}{\partial s}\right)_v = \left(\left(\frac{\partial s}{\partial T}\right)_v\right)^{-1} = \frac{T}{C_v}$$

Since we know $C_p > C_v$ then it follows that $T/C_v > T/C_p$ and therefore

$$\left(\frac{\partial T}{\partial s}\right)_v > \left(\frac{\partial T}{\partial s}\right)_P$$

which means that constant v-lines are steeper than constant P lines in a T-s diagram.

13.37

Derive expressions for $(\partial T/\partial v)_u$ and for $(\partial h/\partial s)_v$ that do not contain the properties *h*, *u*, or *s*. Use Eq. 13.30 with du = 0.

$$\left(\frac{\partial T}{\partial v}\right)_u = -\left(\frac{\partial u}{\partial v}\right)_T \Big/ \left(\frac{\partial u}{\partial T}\right)_v = \frac{P - T\left(\frac{\partial P}{\partial T}\right)_v}{C_v} \qquad \text{(see Eqs. 13.33 and 13.34)}$$

As dh = Tds + vdP => $\left(\frac{\partial h}{\partial s}\right)_v = T + v\left(\frac{\partial P}{\partial s}\right)_v = T - v\left(\frac{\partial T}{\partial v}\right)_s$ (Eq.13.20)

But $\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial s}{\partial v}\right)_T \Big/ \left(\frac{\partial s}{\partial T}\right)_v = -\frac{T\left(\frac{\partial P}{\partial T}\right)_v}{C_v}$ (Eq.13.22)

$$\Rightarrow \qquad \left(\frac{\partial h}{\partial s}\right)_v = T + \frac{vT}{C_v}\left(\frac{\partial P}{\partial T}\right)_v$$

13.38

Develop an expression for the variation in temperature with pressure in a constant entropy process, $(\partial T/\partial P)_s$, that only includes the properties *P–v–T* and the specific heat, C_p. Follow the development for Eq.13.32.

$$\left(\frac{\partial T}{\partial P}\right)_s = -\frac{\left(\frac{\partial s}{\partial P}\right)_T}{\left(\frac{\partial s}{\partial T}\right)_P} = -\frac{-\left(\frac{\partial v}{\partial T}\right)_P}{(C_P/T)} = \frac{T}{C_P}\left(\frac{\partial v}{\partial T}\right)_P$$

$\left\{ \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P\right.$, Maxwell relation Eq. 13.23 and the other is Eq.13.27$\left.\right\}$

13.39

Use Eq. 13.34 to get an expression for the derivative $(\partial T/\partial v)_s$. What is the general shape of a constant s process curve in a T-v diagram? For an ideal gas can you say a little more about the shape?

Equation 13.34 says

$$ds = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_v dv$$

so then in a constant s process we have ds = 0 and we find

$$\left(\frac{\partial T}{\partial v}\right)_s = -\frac{T}{C_v}\left(\frac{\partial P}{\partial T}\right)_v$$

As T is higher the slope is steeper (but negative) unless the last term $(\partial P/\partial T)_v$ counteracts. If we have an ideal gas this last term can be determined

$$P = RT/v \quad \Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\frac{T}{C_v}\frac{R}{v} = -\frac{P}{C_v}$$

and we see the slope is steeper for higher P and a little lower for higher T as C_v is an increasing function of T.

13.40

Evaluate the isothermal changes in the internal energy, the enthalpy and the entropy for an ideal gas. Confirm the results in Chapters 5 and 8.

We need to evaluate du_T, dh_T and ds_T for an ideal gas: $P = RT/v$.

From Eq.13.31 we get

$$du_T = [\ T\ \left(\frac{\partial P}{\partial T}\right)_v - P\ ]\ dv_T = [\ T\ (\frac{R}{v}) - P\ ]\ dv_T = [\ P - P]\ dv_T = 0$$

From Eq.13.27 we get using $v = RT/P$

$$dh_T = [\ v - T\ \left(\frac{\partial v}{\partial T}\right)_P\ ]\ dP_T = [\ v - T\ (\frac{R}{P})\ ]\ dP_T = [\ v - v\ ]\ dP_T = 0$$

These two equations confirms the statements in chapter 5 that u and h are functions of T only for an ideal gas.

From eq.13.32 or Eq.13.34 we get

$$ds_T = -\left(\frac{\partial v}{\partial T}\right)_P dP_T = \left(\frac{\partial P}{\partial T}\right)_v dv_T$$

$$= -\frac{R}{P}\, dP_T = \frac{R}{v}\, dv_T$$

so the change in s can be integrated to find

$$s_2 - s_1 = -R \ln \frac{P_2}{P_1} = R \ln \frac{v_2}{v_1} \qquad \text{when } T_2 = T_1$$

Volume Expansivity and Compressibility

13.41

Determine the volume expansivity, α_P, and the isothermal compressibility, β_T, for water at 20°C, 5 MPa and at 300°C, and 15 MPa using the steam tables.

Water at 20°C, 5 MPa (compressed liquid)

$$\alpha_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \approx \frac{1}{v}\left(\frac{\Delta v}{\Delta T}\right)_P \qquad \text{Estimate by finite difference.}$$

Using values at 0°C, 20°C and 40°C,

$$\alpha_P \approx \frac{1}{0.000\,9995}\,\frac{0.001\,0056 - 0.000\,9977}{40 - 0} = \mathbf{0.000\,1976\ {}^{o}C^{-1}}$$

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \approx -\frac{1}{v}\left(\frac{\Delta v}{\Delta P}\right)_T$$

Using values at saturation, 5 MPa and 10 MPa,

$$\beta_T \approx -\frac{1}{0.000\,9995}\,\frac{0.000\,9972 - 0.001\,0022}{10 - 0.0023} = \mathbf{0.000\,50\ MPa^{-1}}$$

Water at 300°C, 15 MPa (compressed liquid)

$$\alpha_P \approx \frac{1}{0.001\,377}\,\frac{0.001\,4724 - 0.001\,3084}{320 - 280} = \mathbf{0.002\,977\ {}^{o}C^{-1}}$$

$$\beta_T \approx -\frac{1}{0.001\,377}\,\frac{0.001\,3596 - 0.001\,3972}{20 - 10} = \mathbf{0.002\,731\ MPa^{-1}}$$

13.42

What are the volume expansivity α_p, the isothermal compressibility β_T, and the adiabatic compressibility β_s for an ideal gas?

The volume expansivity from Eq.13.37 and ideal gas v = RT/P gives

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\left(\frac{R}{P}\right) = \frac{1}{T}$$

The isothermal compressibility from Eq.13.38 and ideal gas gives

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\left(-RT\,P^{-2}\right) = \frac{1}{P}$$

The adiabatic compressibility β_s from Eq.13.40 and ideal gas

$$\beta_s = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s$$

From Eq.13.32 we get for constant s (ds = 0)

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_P = \frac{T}{C_p}\frac{R}{P} = \frac{v}{C_p}$$

and from Eq.13.34 we get

$$\left(\frac{\partial v}{\partial T}\right)_s = -\frac{C_v}{T}\left(\frac{\partial P}{\partial T}\right)_v = -\frac{C_v}{T}\frac{v}{R} = -\frac{C_v}{P}$$

Finally we can form the desired derivative

$$\left(\frac{\partial v}{\partial P}\right)_s = \left(\frac{\partial v}{\partial T}\right)_s\left(\frac{\partial T}{\partial P}\right)_s = -\frac{C_v}{P}\frac{v}{C_p} = -\frac{v}{kP}$$

$$\beta_s = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s = \left(-\frac{1}{v}\right)\left(-\frac{v}{kP}\right) = \frac{1}{kP} = \frac{1}{k}\,\beta_T$$

13.43

Find the speed of sound for air at 20°C, 100 kPa using the definition in Eq. 13.43 and relations for polytropic processes in ideal gases.

From problem 13.14 : $c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s = -v^2\left(\frac{\partial P}{\partial v}\right)_s$

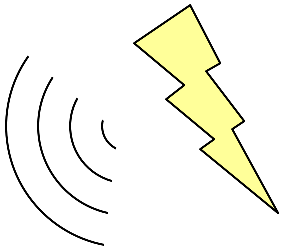
For ideal gas and isentropic process, Pv^k = constant

$$P = Cv^{-k} \;\Rightarrow\; \frac{\partial P}{\partial v} = -kCv^{-k-1} = -kPv^{-1}$$

$$c^2 = -v^2(-kPv^{-1}) = kPv = kRT$$

$$c = \sqrt{kRT} = \sqrt{1.4\times0.287\times293.15\times1000} = \mathbf{343.2\ m/s}$$

For every 3 seconds after the lightning the sound travels about 1 km.



13.44

Assume a substance has uniform properties in all directions with $V = L_x L_y L_z$ and show that volume expansivity $\alpha_p = 3\delta_T$. Hint: differentiate with respect to T and divide by V.

$$V = L_x L_y L_z$$

From Eq.13.37

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{L_x L_y L_z}\left(\frac{\partial\, L_x L_y L_z}{\partial T}\right)_P$$

$$= \frac{L_y L_z}{L_x L_y L_z}\left(\frac{\partial\, L_x}{\partial T}\right)_P + \frac{L_x L_z}{L_x L_y L_z}\left(\frac{\partial\, L_y}{\partial T}\right)_P + \frac{L_x L_y}{L_x L_y L_z}\left(\frac{\partial\, L_z}{\partial T}\right)_P$$

$$= \frac{1}{L_x}\left(\frac{\partial\, L_x}{\partial T}\right)_P + \frac{1}{L_y}\left(\frac{\partial\, L_y}{\partial T}\right)_P + \frac{1}{L_z}\left(\frac{\partial\, L_z}{\partial T}\right)_P$$

$$= 3\ \delta_T$$

This of course assumes isotropic properties (the same in all directions).

13.45

A cylinder fitted with a piston contains liquid methanol at 20°C, 100 kPa and volume 10 L. The piston is moved, compressing the methanol to 20 MPa at constant temperature. Calculate the work required for this process. The isothermal compressibility of liquid methanol at 20°C is 1.22×10^{-9} m^2/N.

$$_1w_2 = \int_1^2 P dv = \int P \left(\frac{\partial v}{\partial P}\right)_T dP_T = -\int_1^2 v\beta_T P dP_T$$

For v ≈ constant & β_T ≈ constant the integral can be evaluated

$$_1w_2 = -\frac{v\beta_T}{2}\left(P_2^2 - P_1^2\right)$$

For liquid methanol, from Table A.4: $\rho = 787$ m^3/kg

$V_1 = 10$ L, $m = 0.01 \times 787 = 7.87$ kg

$$_1W_2 = \frac{0.01 \times 1220}{2}\left[(20)^2 - (0.1)^2\right] = 2440 \text{ J} = \mathbf{2.44\ kJ}$$

13.46

Use Eq. 13.32 to solve for $(\partial T/\partial P)_s$ in terms of T, v, C_p and α_p. How large a temperature change does 25°C water ($\alpha_p = 2.1 \times 10^{-4}\ K^{-1}$) have, when compressed from 100 kPa to 1000 kPa in an isentropic process?

From Eq.13.32 we get for constant s (ds = 0) and Eq.13.37

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_P = \frac{T}{C_p}\alpha_p\, v$$

Assuming the derivative is constant for the isentropic compression we estimate with heat capacity from Table A.3 and v from B.1.1

$$\Delta T_s = \left(\frac{\partial T}{\partial P}\right)_s \Delta P_s = \frac{T}{C_p}\alpha_p\, v\, \Delta P_s$$

$$= \frac{273.15 + 25}{4.18} \times 2.1 \times 10^{-4} \times 0.001003 \times (1000 - 100)$$

= **0.013 K** barely measurable.

13.47

Sound waves propagate through a media as pressure waves that cause the media to go through isentropic compression and expansion processes. The speed of sound c is defined by $c^2 = (\partial P/\partial \rho)_s$ and it can be related to the adiabatic compressibility, which for liquid ethanol at 20°C is 9.4×10^{-10} m^2/N. Find the speed of sound at this temperature.

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s = -v^2\left(\frac{\partial P}{\partial v}\right)_s = \frac{1}{-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s \rho} = \frac{1}{\beta_s \rho}$$

From Table A.4 for ethanol, $\rho = 783 \text{ kg/m}^3$

$$\Rightarrow \qquad c = \left(\frac{1}{940\times10^{-12}\times783}\right)^{1/2} = \mathbf{1166\ m/s}$$

13.48

For commercial copper at 25°C (see table A.3) the speed of sound is about 4800 m/s. What is the adiabatic compressibility β_s?

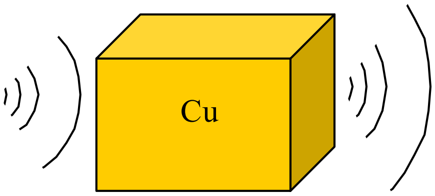
From Eq.13.43 and Eq.13.40

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s = -v^2\left(\frac{\partial P}{\partial v}\right)_s = \frac{1}{-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s \rho} = \frac{1}{\beta_s \rho}$$

Then we get using density from Table A.3

$$\beta_s = \frac{1}{c^2\rho} = \frac{1}{4800^2 \times 8300}\ \frac{s^2\ m^3}{m^2\ kg} = \frac{1000}{4800^2 \times 8300}\ \frac{1}{kPa}$$

$$\boldsymbol{= 5.23 \times 10^{-9}\ \ kPa^{-1}}$$



13.49

Consider the speed of sound as defined in Eq. 13.43. Calculate the speed of sound for liquid water at 20°C, 2.5 MPa, and for water vapor at 200°C, 300 kPa, using the steam tables.

From Eq. 13.43: $c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s = -v^2\left(\frac{\partial P}{\partial v}\right)_s$

Liquid water at 20°C, 2.5 MPa, assume

$$\left(\frac{\partial P}{\partial v}\right)_s \approx \left(\frac{\Delta P}{\Delta v}\right)_T$$

Using saturated liquid at 20°C and compressed liquid at 20°C, 5 MPa,

$$c^2 = -\left(\frac{0.001\,002+0.000\,9995}{2}\right)^2\left(\frac{5-0.0023}{0.000\,9995-0.001\,002}\right) = 2.002\times10^6$$

=> c = **1415 m/s**

Superheated vapor water at 200°C, 300 kPa

$v = 0.7163$ m^3/kg, $s = 7.3115$ kJ/kg K

At P = 200 kPa & s = 7.3115 kJ/kg K: T = 157°C, $v = 0.9766$ m^3/kg

At P = 400 kPa & s = 7.3115 kJ/kg K: T = 233.8°C, $v = 0.5754$ m^3/kg

$$c^2 = -(0.7163)^2\left(\frac{0.400-0.200}{0.5754-0.9766}\right) = 0.2558 \times 10^6 \text{ m}^2/\text{s}^2$$

=> c = **506 m/s**

13.50

Soft rubber is used as a part of a motor mounting. Its adiabatic bulk modulus is $B_s = 2.82 \times 10^6$ kPa, and the volume expansivity is $\alpha_p = 4.86 \times 10^{-4}$ K^{-1}. What is the speed of sound vibrations through the rubber, and what is the relative volume change for a pressure change of 1 MPa?

From Eq.13.43 and Eq.13.40

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s = -v^2\left(\frac{\partial P}{\partial v}\right)_s = \frac{1}{-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s \rho} = \frac{1}{\beta_s \rho} = \frac{B_s}{\rho}$$

$$= 2.82 \times 10^6 \times 1000 \text{ Pa} / 1100 \text{ kg/m}^3 = 2.564 \times 10^6 \text{ m}^2/\text{s}^2$$

c = 1601 m/s

If the volume change is fast it is isentropic and if it is slow it is isothermal. We will assume it is isentropic

$$\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_s = -\beta_s = -\frac{1}{B_s}$$

then

$$\frac{\Delta V}{V} = -\frac{\Delta P}{B_s} = -\frac{1000}{2.82 \times 10^6} = \mathbf{-3.55 \times 10^{-4}}$$

13.51

Liquid methanol at 25°C has an adiabatic compressibility of 1.05×10^{-9} m^2/N. What is the speed of sound? If it is compressed from 100 kPa to 10 MPa in an insulated piston/cylinder, what is the specific work?

From Eq.13.43 and Eq.13.40 and the density from table A.4

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s = -v^2\left(\frac{\partial P}{\partial v}\right)_s = \frac{1}{\beta_s \rho} = \frac{1}{1.05 \times 10^{-9} \times 787}$$

$$= 1.210 \times 10^6 \ m^2/s^2$$

$$c = \mathbf{1100\ m/s}$$

The specific work becomes

$$w = \int P\, dv = \int P\, (-\beta_s v)\, dP = -\int \beta_s v\, P\, dP = -\beta_s\, v \int_1^2 P\, dP$$

$$= -\beta_s\, v\, 0.5\, (P_2^2 - P_1^2)$$

$$= -1.05 \times 10^{-9}\ m^2/N \times \frac{0.5}{787}\ m^3/kg \times (10\,000^2 - 100^2) \times 1000^2\ Pa^2$$

$$= \mathbf{-66.7\ J/kg}$$

13.52

Use Eq. 13.32 to solve for $(\partial T/\partial P)_s$ in terms of T, v, C_p and α_p. How much higher does the temperature become for the compression of the methanol in Problem 13.51? Use $\alpha_p = 2.4 \times 10^{-4}\ \mathrm{K}^{-1}$ for methanol at 25°C.

From Eq.13.32 we get for constant s (ds = 0) and Eq.13.37

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_P = \frac{T}{C_p}\,\alpha_p\, v$$

Assuming the derivative is constant for the isentropic compression we estimate with heat capacity and density (v = 1/ρ) from Table A.4

$$\Delta T_s = \left(\frac{\partial T}{\partial P}\right)_s \Delta P_s = \frac{T}{C_p}\,\alpha_p\, v\, \Delta P_s$$

$$= \frac{298.15}{2.55}\,\frac{\mathrm{K\ kg\ K}}{\mathrm{kJ}} \times 2.4 \times 10^{-4}\ \mathrm{K}^{-1} \times \frac{1}{787}\,\frac{\mathrm{m}^3}{\mathrm{kg}} \times (10\,000 - 100)\ \mathrm{kPa}$$

= **0.353 K**

Equations of State

13.53

Use the equation of state as shown in Example 13.3 where changes in enthalpy and entropy were found. Find the isothermal change in internal energy in a similar fashion; do not compute it from enthalpy.

The equation of state is

$$\frac{Pv}{RT} = 1 - C' \frac{P}{T^4}$$

and to integrate for changes in u from eq.13.31 we it explicit in P as

$$P = T^4 \left(\frac{v}{R} T^3 + C' \right)^{-1}$$

Now perform the partial derivative of P

$$\left(\frac{\partial P}{\partial T}\right)_v = 4\, T^3 \left(\frac{v}{R} T^3 + C' \right)^{-1} - T^4 \left(\frac{v}{R} T^3 + C' \right)^{-2} 3 \frac{v}{R} T^2$$

$$= 4 \frac{P}{T} - \frac{P^2}{T^4} 3 \frac{v}{R} T^2 = 4 \frac{P}{T} - 3 \frac{P}{T} \times \frac{Pv}{RT} = \frac{P}{T} \left[4 - 3 \frac{Pv}{RT} \right]$$

Substitute into Eq.13.31

$$du_T = \left[T \left(\frac{\partial P}{\partial T}\right)_v - P \right] dv_T = \left[P\left(4 - 3 \frac{Pv}{RT}\right) - P \right] dv_T$$

$$= 3\, P \left(1 - \frac{Pv}{RT}\right)\ dv_T = 3\, P\, C' \frac{P}{T^4}\ dv_T$$

The P must be eliminated in terms of v or the opposite, we do the latter as from the equation of state

$$v = \frac{RT}{P} - C'\, R \frac{1}{T^3} \qquad \Rightarrow \qquad dv_T = -\frac{RT}{P^2}\, dP_T$$

so now

$$du_T = 3\, C' \frac{P^2}{T^4}\, dv_T = - 3\, C'\, R \frac{1}{T^3}\ dP_T$$

and the integration becomes

$$u_2 - u_1 = - 3\, C'\, R\, T^{-3} (P_2 - P_1)$$

13.54

Evaluate changes in an isothermal process for u, h and s for a gas with an equation of state as $P(v - b) = RT$.

From Eq.13.31 we get

$$du_T = \left[T \left(\frac{\partial P}{\partial T}\right)_v - P \right] dv_T = \left[T \left(\frac{R}{v - b}\right) - P \right] dv_T = [P - P] dv_T = 0$$

From Eq.13.27 we get using $v = b + RT/P$

$$dh_T = \left[v - T \left(\frac{\partial v}{\partial T}\right)_P \right] dP_T = \left[v - T \left(\frac{R}{P}\right) \right] dP_T = b\, dP_T$$

From eq.13.32 or Eq.13.34 we get

$$ds_T = -\left(\frac{\partial v}{\partial T}\right)_P dP_T = \left(\frac{\partial P}{\partial T}\right)_v dv_T$$

$$= -\frac{R}{P} dP_T = \frac{R}{v - b} dv_T$$

Now the changes in u, h and s can be integrated to find

$$u_2 - u_1 = 0$$

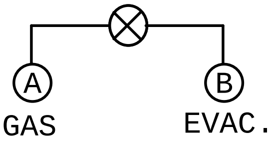
$$h_2 - h_1 = \int b\, dP = b(P_2 - P_1)$$

$$s_2 - s_1 = -R \ln \frac{P_2}{P_1} = R \ln \frac{v_2 - b}{v_1 - b}$$

13.55

Two uninsulated tanks of equal volume are connected by a valve. One tank contains a gas at a moderate pressure P_1, and the other tank is evacuated. The valve is opened and remains open for a long time. Is the final pressure P_2 greater than, equal to, or less than $P_1/2$? Hint: Recall Fig. 13.5.

Assume the temperature stays constant then for an ideal gas the pressure will be reduced to half the original pressure. For the real gas the compressibility factor maybe different from 1 and then changes towards one as the pressure drops.

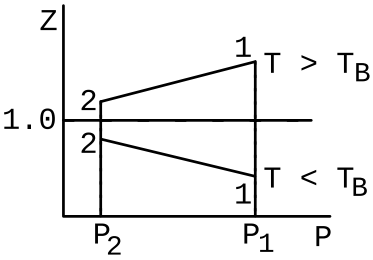


$$V_A = V_B \;\Rightarrow\; V_2 = 2V_1, \quad T_2 = T_1 = T$$

$$\frac{P_2}{P_1} = \frac{V_1}{V_2}\,\frac{Z_2}{Z_1}\,\frac{mRT}{mRT} = \frac{1}{2}\,\frac{Z_2}{Z_1}$$

$$\text{If } T < T_B, \quad Z_2 > Z_1 \;\Rightarrow\; \frac{P_2}{P_1} > \frac{1}{2}$$

$$\text{If } T > T_B, \quad Z_2 < Z_1 \;\Rightarrow\; \frac{P_2}{P_1} < \frac{1}{2}$$



13.56

Determine the reduced Boyle temperature as predicted by an equation of state (the experimentally observed value for most substances is about 2.5), using the van der Waals equation and the Redlich–Kwong equation. Note: It is helpful to use Eqs. 13.47 and 13.48 in addition to Eq. 13.46

The Boyle temp. is that T at which $\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = 0$

But $\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = \lim_{P\to 0}\frac{Z-1}{P-0} = \frac{1}{RT}\lim_{P\to 0}\left(v - \frac{RT}{P}\right)$

van der Waals: $P = \frac{RT}{v-b} - \frac{a}{v^2}$

multiply by $\frac{v-b}{P}$, get

$$v-b = \frac{RT}{P} - \frac{a(v-b)}{Pv^2} \quad \text{or} \quad v - \frac{RT}{P} = b - \frac{a(1-b/v)}{Pv}$$

$$\& \quad RT \times \lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = b - \frac{a(1-0)}{RT} = 0 \quad \text{only at } T_{Boyle}$$

$$\text{or} \quad T_{Boyle} = \frac{a}{Rb} = \frac{27}{8}T_C = \mathbf{3.375\, T_C}$$

Redlich-Kwong: $P = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{1/2}}$

as in the first part, get

$$v - \frac{RT}{P} = b - \frac{a(1-b/v)}{Pv(1+b/v)T^{1/2}}$$

$$\& \; RT \times \lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = b - \frac{a(1-0)}{Pv(1+0)T^{1/2}} = 0 \quad \text{only at } T_{Boyle}$$

$$\text{or} \quad T_{Boyle}^{3/2} = \frac{a}{Rb} = \frac{0.427\,48\, R^2 T_C^{5/2}}{RP_C} \times \frac{P_C}{0.08\,664\, R\, T_C}$$

$$T_{Boyle} = \left(\frac{0.427\,48}{0.086\,64}\right)^{2/3} T_C = \mathbf{2.9\, T_C}$$

13.57

Develop expressions for isothermal changes in internal energy, enthalpy and entropy for a gas obeying the van der Waals equation of state.

van der Waals equation of state: $P = \frac{RT}{v-b} - \frac{a}{v^2}$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2}$$

$$(u_2-u_1)_T = \int_1^2 [T\left(\frac{\partial P}{\partial T}\right)_v - P]dv = \int_1^2 \frac{a}{v^2}dv = a(\frac{1}{v_1} - \frac{1}{v_2})$$

$$(h_2-h_1)_T = (u_2-u_1)_T + P_2v_2 - P_1v_1 = P_2v_2 - P_1v_1 + a(\frac{1}{v_1} - \frac{1}{v_2})$$

$$(s_2-s_1)_T = \int_1^2 \left(\frac{\partial P}{\partial T}\right)_v dv = \int_1^2 \frac{R}{v-b} dv = R \ln\left(\frac{v_2-b}{v_1-b}\right)$$

13.58

Develop expressions for isothermal changes in internal energy, enthalpy and entropy for a gas obeying Redlich-Kwong equation of state.

Redlich-Kwong equation of state: $P = \frac{RT}{v - b} - \frac{a}{v(v + b)T^{1/2}}$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v - b} + \frac{a}{2v(v + b)T^{3/2}}$$

From eq.13.31

$$(u_2 - u_1)_T = \int_1^2 \frac{3a}{2v(v + b)T^{1/2}} dv = \frac{-3a}{2bT^{1/2}} \ln\left[\left(\frac{v_2 + b}{v_2}\right)\left(\frac{v_1}{v_1 + b}\right)\right]$$

We find change in h from change in u, so we do not do the derivative in eq.13.27. This is due to the form of the EOS.

$$(h_2 - h_1)_T = P_2v_2 - P_1v_1 - \frac{3a}{2bT^{1/2}} \ln\left[\left(\frac{v_2 + b}{v_2}\right)\left(\frac{v_1}{v_1 + b}\right)\right]$$

Entropy follows from Eq.13.35

$$(s_2 - s_1)_T = \int_1^2 \left[\frac{R}{v - b} + \frac{a/2}{v(v + b)T^{3/2}}\right] dv$$

$$= R \ln\left(\frac{v_2 - b}{v_1 - b}\right) - \frac{a}{2bT^{3/2}} \ln\left[\left(\frac{v_2 + b}{v_2}\right)\left(\frac{v_1}{v_1 + b}\right)\right]$$

13.59

Consider the following equation of state, expressed in terms of reduced pressure and temperature: $Z = 1 + (P_r/14T_r)[1 - 6T_r^{-2}]$. What does this predict for the reduced Boyle temperature?

$$Z = \frac{Pv}{RT} = 1 + \frac{P_r}{14\,T_r}\left(1 - \frac{6}{T_r^2}\right)$$

$$\left(\frac{\partial Z}{\partial P}\right)_T = \frac{1}{14P_cT_r}\left(1 - \frac{6}{T_r^2}\right) \qquad \Rightarrow \qquad \lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = 0 \text{ at } T_{boyle}$$

$$\left(1 - \frac{6}{T_r^2}\right) = 0 \quad \rightarrow \quad T_r = \sqrt{6} = \mathbf{2.45}$$

13.60

What is the Boyle temperature for the following equation of state: $P = \frac{RT}{v\text{-}b} - \frac{a}{v^2T}$ where a and b are constants.

$$P = \frac{RT}{v\text{-}b} - \frac{a}{v^2T}$$

Multiplying by $\frac{v\text{-}b}{P}$ gives: $v - b = \frac{RT}{P} - \frac{a(1\text{-}b/v)}{PvT}$

Using solution from **13.56** for T_{Boyle}:

$$\lim_{P \to 0}\left(v - \frac{RT}{P}\right) = b - \frac{a(1\text{-}0)}{RT \times T} = b - \frac{a}{RT^2} = 0 \text{ at } T_{Boyle}$$

or $T_{Boyle} = \sqrt{\frac{a}{Rb}} = \sqrt{\frac{27}{64}\frac{R^2T_C^3}{P_C}\frac{1}{R}\frac{8P_C}{RT_C}} = \sqrt{\mathbf{\frac{27}{8}}}\,\mathbf{T_C}$

13.61

Show that the van der Waals equation can be written as a cubic equation in the compressibility factor involving the reduced pressure and reduced temperature as

$$Z^3 - \left(\frac{P_r}{8T_r} + 1\right) Z^2 + \left(\frac{27\,P_r}{64\,T_r^2}\right) Z - \frac{27\,P_r^{\,2}}{512\,T_r^{\,3}} = 0$$

van der Waals equation, Eq.13.55: $P = \frac{RT}{v\text{-}b} - \frac{a}{v^2}$

$$a = \frac{27}{64}\frac{R^2T_C^{\,2}}{P_C} \qquad b = \frac{RT_C}{8P_C}$$

multiply equation by $\frac{v^2(v\text{-}b)}{P}$

Get: $v^3 - (b + \frac{RT}{P})\, v^2 + (\frac{a}{P})\, v - \frac{ab}{P} = 0$

Multiply by $\frac{P^3}{R^3\,T^3}$ and substitute $Z = \frac{Pv}{RT}$

Get: $Z^3 - (\frac{bP}{RT} + 1)\, Z^2 + (\frac{aP}{R^2T^2})\, Z - (\frac{abP^2}{R^3\,T^3}) = 0$

Substitute for a and b, get:

$$Z^3 - \left(\frac{P_r}{8T_r} + 1\right) Z^2 + \left(\frac{27\,P_r}{64\,T_r^2}\right) Z - \frac{27\,P_r^{\,2}}{512\,T_r^{\,3}} = 0$$

Where $P_r = \frac{P}{P_c}$, $T_r = \frac{T}{T_c}$

13.62

Determine the second virial coefficient B(T) using the van der Waals equation of state. Also find its value at the critical temperature where the experimentally observed value is about –0.34 RT_c/P_c.

From Eq. 13.51: $B(T) = - \lim_{P \to 0} \alpha$ where Eq. 13.47: $\alpha = \frac{RT}{P} - v$

van der Waals: $P = \frac{RT}{v-b} - \frac{a}{v^2}$ which we can multiply by $\frac{v-b}{P}$, get

$$v - b = \frac{RT}{P} - \frac{a(v-b)}{Pv^2} \quad \text{or} \quad v - \frac{RT}{P} = b - \frac{a(1-b/v)}{Pv}$$

Taking the limit for P -> 0 then (Pv -> RT and v -> ∞) we get :

$$B(T) = b - a/RT = \frac{RT_C}{P_C} \left(\frac{1}{8} - \frac{27\ T_C}{64\ T} \right)$$

where a,b are from Eq.13.59. At $T = T_C$ then we have

$$B(T_C) = \frac{RT_C}{P_C} \left(- \frac{19}{64} \right) = -0.297 \frac{RT_C}{P_C}$$

13.63

Determine the second virial coefficient B(T) using the Redlich-Kwong equation of state. Also find its value at the critical temperature where the experimentally observed value is about $-0.34\ RT_c/P_c$.

From Eq.13.51: $B(T) = -\lim_{P\to 0} \alpha$ where Eq.13.47: $\alpha = \frac{RT}{P} - v$

For Redlich Kwong the result becomes

$$v - \frac{RT}{P} = b - \frac{a(1 - b/v)}{Pv(1 + b/v)\ T^{1/2}}$$

Taking the limit for P -> 0 then ($Pv \to RT$ and $v \to \infty$) we get :

$$\Rightarrow \quad B(T) = b - \frac{a}{RT^{3/2}}$$

Now substitute Eqs. 13.61 and 13.62 for a and b,

$$B(T) = \frac{RT_C}{P_C}\left[0.08664 - 0.42748\left(\frac{T_C}{T}\right)^{3/2}\right]$$

and evaluated at T_C it becomes

$$B(T_C) = \frac{RT_C}{P_C}\left[0.08664 - 0.42748\right] = -0.341\ \frac{RT_C}{P_C}$$

13.64

One early attempt to improve on the van der Waals equation of state was an expression of the form

$$P = \frac{RT}{v-b} - \frac{a}{v^2T}$$

Solve for the constants *a*, *b*, and v_C using the same procedure as for the van der Waals equation.

From the equation of state take the first two derivatives of P with v:

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3T} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = -\frac{2RT}{(v-b)^3} - \frac{6a}{v^4T}$$

Since both these derivatives are zero at the critical point:

$$-\frac{RT}{(v-b)^2} + \frac{2a}{v^3T} = 0 \qquad \text{and} \qquad -\frac{2RT}{(v-b)^3} - \frac{6a}{v^4T} = 0$$

Also, $$P_C = \frac{RT_C}{v_C-b} - \frac{a}{v_C^2\,T_C}$$

solving these three equations:

$$v_C = 3b, \quad a = \frac{27}{64}\frac{R^2T_C^3}{P_C}, \qquad b = \frac{RT_C}{8P_C}$$

13.65

Calculate the difference in internal energy of the ideal-gas value and the real-gas value for carbon dioxide at the state 20°C, 1 MPa, as determined using the virial equation of state, including second virial coefficient terms. For carbon dioxide we have: B = -0.128 m^3/kmol, T(dB/dT) = 0.266 m^3/kmol, both at 20°C.

virial eq.: $$P = \frac{RT}{v} + \frac{BRT}{v^2} \;; \qquad \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v} + \frac{BR}{v^2} + \frac{RT}{v^2}\left(\frac{dB}{dT}\right)$$

$$u\text{-}u^* = -\int_\infty^v \left[\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv = -\int_\infty^v \left[\frac{RT^2}{v^2}\left(\frac{dB}{dT}\right)\right]dv = -\frac{RT}{v}\left[T\left(\frac{dB}{dT}\right)\right]$$

Solution of virial equation (quadratic formula):

$$\bar{v} = \frac{1}{2}\frac{\bar{R}T}{P}\left[1 + \sqrt{1 + 4BP/\bar{R}T}\,\right] \qquad \text{where: } \frac{\bar{R}T}{P} = \frac{8.3145 \times 293.15}{1000} = 2.43737$$

$$\bar{v} = \frac{1}{2} \times 2.43737 \left[1 + \sqrt{1 + 4(-0.128)/2.43737}\,\right] = 2.3018 \text{ m}^3\text{/kmol}$$

Using the minus-sign root of the quadratic formula results in a compressibility factor < 0.5, which is not consistent with such a truncated equation of state.

$$u\text{-}u^* = \frac{-8.3145 \times 293.15}{2.3018}\left[0.266\right] = \mathbf{-\ 281.7\ kJ/kmol}$$

13.66

Calculate the difference in entropy of the ideal-gas value and the real-gas value for carbon dioxide at the state 20°C, 1 MPa, as determined using the virial equation of state. Use numerical values given in Problem 13.65.

CO_2 at $T = 20^oC$, $P = 1$ MPa

$$s^*_{P^*} - s_P = \int_{v(P)}^{RT/P^*} \left(\frac{\partial P}{\partial T}\right)_v dv \;;\quad \text{ID Gas,} \qquad s^*_{P^*} - s_P = \int_{v(P)}^{RT/P^*} \frac{R}{v} dv = R \ln \frac{P}{P^*}$$

Therefore, at P: $$s^*_P - s_P = -R \ln \frac{P}{P^*} + \int_{v(P)}^{RT/P^*} \left(\frac{\partial P}{\partial T}\right)_v dv$$

virial: $$P = \frac{RT}{v} + \frac{BRT}{v^2} \quad \text{and} \quad \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v} + \frac{BR}{v^2} + \frac{RT}{v^2}\left(\frac{dB}{dT}\right)$$

Integrating,

$$s^*_P - s_P = -R \ln \frac{P}{P^*} + R \ln \frac{RT}{P^* v} + R\left[B + T\left(\frac{dB}{dT}\right)\right]\left(\frac{1}{v} - \frac{P^*}{RT}\right)$$

$$= R\left[\ln \frac{RT}{Pv} + \left(B + T\left(\frac{dB}{dT}\right)\right)\frac{1}{v}\right]$$

Using values for CO_2 from solution 13.65,

$$\bar{s}^*_P - \bar{s}_P = 8.3145\left[\ln \frac{2.437\,37}{2.3018} + \left(-0.128 + 0.266\right)\frac{1}{2.3018}\right]$$

$$= \mathbf{0.9743\ kJ/kmol\ K}$$

13.67

A rigid tank contains 1 kg oxygen at 160 K, 4 MPa. Determine the volume of the tank assuming we can use the Redlich-Kwong equation of state for oxygen. Compare the result with the ideal gas law.

For the ideal gas law: $Pv = RT$ so $v = RT/P$

$v = 0.2598 \times 160 / 4000 = 0.0104\ \text{m}^3/\text{kg}$; $V = mv =$ $\mathbf{0.0104\ m^3}$

For Redlich-Kwong, Eq.13.57 and oxygen

$P_c = 5040$ kPa; $T_c = 154.6$ K; $R = 0.2598$ kJ/kg K

$$b = 0.08664 \frac{RT_c}{P_c} = 0.08664 \times \frac{0.2598 \times 154.6}{5040} = 0.000\,690\,5\ \text{m}^3/\text{kg}$$

$$a = 0.427\,48 \frac{R^2T_c^{5/2}}{P_c} = 0.427\,48 \times \frac{0.2598^2 \times 154.6^{5/2}}{5040} = 1.7013$$

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)T^{1/2}}$$ trial and error to get v due to nonlinearity

$v = 0.01\ \text{m}^3/\text{kg} \Rightarrow$ $P = 4465.1 - 1279.9 = 3185.2$ kPa too low

$v = 0.008\ \text{m}^3/\text{kg} \Rightarrow$ $P = 5686.85 - 1968.1 = 3718.8$ kPa too low

$v = 0.0075\ \text{m}^3/\text{kg} \Rightarrow$ $P = 6104.41 - 2227.43 = 3876.98$ kPa

$v = 0.007\ \text{m}^3/\text{kg} \Rightarrow$ $P = 6588.16 - 2541.70 = 4046.46$ kPa

Now we interpolate between the last two entries and check

$v = 0.00714\ \text{m}^3/\text{kg} \Rightarrow P = 6445.15 - 2447.3 = 3997.8$ kPa OK

$V = mv =$ $\mathbf{0.00714\ m^3}$ (69% of the ideal gas value)

13.68

A flow of oxygen at 230 K, 5 MPa is throttled to 100 kPa in a steady flow process. Find the exit temperature and the specific entropy generation using Redlich-Kwong equation of state and ideal gas heat capacity. Notice that this becomes iterative due to the nonlinearity coupling h, P, v and T.

C.V. Throttle. Steady single flow, no heat transfer and no work.

Energy eq.: $h_1 + 0 = h_2 + 0$ so constant h

Entropy Eq.: $s_1 + s_{gen} = s_2$ so entropy generation

Find the change in h from Eq.13.26 assuming C_p is constant.

Redlich-Kwong equation of state: $P = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{1/2}}$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} + \frac{a}{2v(v+b)T^{3/2}}$$

From eq.13.31

$$(u_2 - u_1)_T = \int_1^2 \frac{3a}{2v(v+b)T^{1/2}}\,dv = \frac{-3a}{2bT^{1/2}} \ln\left[\left(\frac{v_2+b}{v_2}\right)\left(\frac{v_1}{v_1+b}\right)\right]$$

We find change in h from change in u, so we do not do the derivative in eq.13.27. This is due to the form of the EOS.

$$(h_2 - h_1)_T = P_2v_2 - P_1v_1 - \frac{3a}{2bT^{1/2}} \ln\left[\left(\frac{v_2+b}{v_2}\right)\left(\frac{v_1}{v_1+b}\right)\right]$$

Entropy follows from Eq.13.35

$$(s_2 - s_1)_T = \int_1^2 \left[\frac{R}{v-b} + \frac{a/2}{v(v+b)T^{3/2}}\right] dv$$

$$= R \ln\left(\frac{v_2-b}{v_1-b}\right) - \frac{a}{2bT^{3/2}} \ln\left[\left(\frac{v_2+b}{v_2}\right)\left(\frac{v_1}{v_1+b}\right)\right]$$

$P_c = 5040$ kPa; $T_c = 154.6$ K; $R = 0.2598$ kJ/kg K

$$b = 0.08664 \frac{RT_c}{P_c} = 0.08664 \times \frac{0.2598 \times 154.6}{5040} = 0.000\,690\,5 \text{ m}^3\text{/kg}$$

$$a = 0.427\,48\,\frac{R^2T_c^{5/2}}{P_c} = 0.427\,48 \times \frac{0.2598^2 \times 154.6^{5/2}}{5040} = 1.7013$$

We need to find T_2 so the energy equation is satisfied

$$h_2 - h_1 = h_2 - h_x + h_x - h_1 = C_p(T_2 - T_1) + (h_2 - h_1)_T = 0$$

and we will evaluate it similar to Fig. 13.4, where the first term is done from state x to 2 and the second term is done from state 1 to state x (at $T_1 = 230$ K). We do this as we assume state 2 is close to ideal gas, but we do not know T_2.

We first need to find v_1 from the EOS, so guess v and find P

$v_1 = 0.011\ m^3/kg \quad \Rightarrow \quad P = 5796.0 - 872.35 = 4924$ too low

$v_1 = 0.01082\ m^3/kg \quad \Rightarrow \quad P = 5899.0 - 900.7 = 4998.3$ OK

Now evaluate the change in h along the 230 K from state 1 to state x, that requires a value for v_x. Guess ideal gas at $T_x = 230$ K,

$$v_x = RT_x/P_2 = 0.2598 \times 230/100 = 0.59754\ m^3/kg$$

From the EOS: $P_2 = 100.1157 - 0.3138 = 99.802$ kPa (close)

A few more guesses and adjustments gives

$v_x = 0.59635\ m^3/kg;\quad P_2 = 100.3157 - 0.3151 = 100.0006$ kPa OK

$$(h_x - h_1)_T = P_xv_x - P_1v_1 - \frac{3a}{2bT^{1/2}}\ln\left[\left(\frac{v_x + b}{v_x}\right)\left(\frac{v_1}{v_1 + b}\right)\right]$$

$$= 59.635 - 5000 \times 0.01082 - 243.694\ \ln\left[\frac{0.59704}{0.59635} \times \frac{0.01082}{0.01151}\right]$$

$$= 59.635 - 54.1 + 14.78335 = 20.318\ kJ/kg$$

From energy eq.: $T_2 = T_1 - (h_x - h_1)_T/C_p = 230 - 20.318 / 0.922 =$ **208 K**

Now the change in s is done in a similar fashion,

$$s_{gen} = s_2 - s_1 = (s_x - s_1)_T + s_2 - s_x$$

$$= R\ln\left(\frac{v_x - b}{v_1 - b}\right) - \frac{a}{2bT^{3/2}}\ln\left[\left(\frac{v_x + b}{v_x}\right)\left(\frac{v_1}{v_1 + b}\right)\right] + C_p \ln\frac{T_2}{T_x}$$

$$= 0.2598\ \ln\left(\frac{0.59566}{0.0101295}\right) - 0.35318\ \ln(0.94114) + 0.922\ \ln\left(\frac{208}{230}\right)$$

$$= 1.05848 + 0.021425 - 0.092699$$

$$= \mathbf{0.987\ kJ/kg\ K}$$

Generalized Charts

13.69

A 200-L rigid tank contains propane at 9 MPa, 280°C. The propane is then allowed to cool to 50°C as heat is transferred with the surroundings. Determine the quality at the final state and the mass of liquid in the tank, using the generalized compressibility chart, Fig. D.1.

Propane C_3H_8: $V = 0.2\ m^3$, $P_1 = 9$ MPa, $T_1 = 280^oC = 553.2$ K

cool to $T_2 = 50\ ^oC = 323.2$ K

From Table A.2: $T_C = 369.8$ K, $P_C = 4.25$ MPa

$$P_{r1} = \frac{9}{4.25} = 2.118, \quad T_{r1} = \frac{553.2}{369.8} = 1.496 \qquad \text{From Fig. D.1:} \quad Z_1 = 0.825$$

$$v_2 = v_1 = \frac{Z_1RT_1}{P_1} = \frac{0.825\times0.188\ 55\times553.2}{9\ 000} = 0.00956\ m^3/kg$$

From Fig. D.1 at $T_{r2} = 0.874$,

$P_{G2} = 0.45 \times 4250 = 1912$ kPa

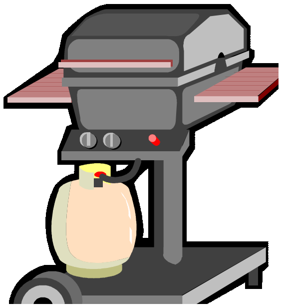
$v_{G2} = 0.71 \times 0.188\ 55 \times 323.2/1912 = 0.02263\ m^3/kg$

$v_{F2} = 0.075 \times 0.188\ 55 \times 323.2/1912 = 0.00239\ m^3/kg$

$0.00956 = 0.002\ 39 + x_2(0.02263 - 0.00239)$ => $x_2 = \mathbf{0.354}$

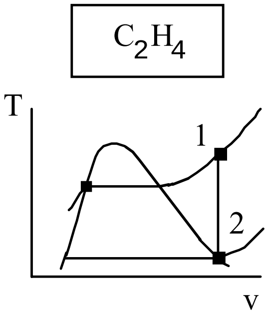
$m_{LIQ\ 2} = (1\text{-}0.354)\times0.2/0.00956 = \mathbf{13.51\ kg}$

These tanks
contain liquid
propane.



13.70

A rigid tank contains 5 kg of ethylene at 3 MPa, 30°C. It is cooled until the ethylene reaches the saturated vapor curve. What is the final temperature?



V = const   m = 5 kg

P_1 = 3 MPa T_1 = 30 °C = 303.2 K

cool to x_2 = 1.0

$$P_{r1} = \frac{3}{5.04} = 0.595, \quad T_{r1} = \frac{303.2}{282.4} = 1.074$$

Fig. D.1: Z_1 = 0.82

$$P_{r2} = P_{r1}\frac{Z_2 T_{r2}}{Z_1 T_{r1}} = 0.595\frac{Z_{G2} T_{r2}}{0.82 \times 1.074} = 0.6756\, Z_{G2} T_{r2}$$

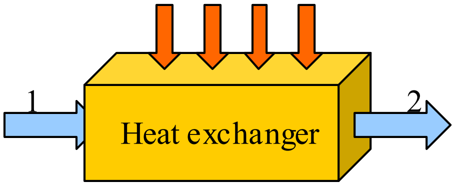
Trial & error:

T_{r2}	Z_{G2}	P_{r2}	$P_{r2\ CALC}$		
0.866	0.72	0.42	0.421	~ OK	=> T_2 = **244.6 K**

13.71

Refrigerant-123, dichlorotrifluoroethane, which is currently under development as a potential replacement for environmentally hazardous refrigerants, undergoes an isothermal steady flow process in which the R-123 enters a heat exchanger as saturated liquid at 40°C and exits at 100 kPa. Calculate the heat transfer per kilogram of R-123, using the generalized charts, Fig. D.2

R-123: $M = 152.93$, $T_C = 456.9$ K, $P_C = 3.67$ MPa



$T_1 = T_2 = 40\ ^oC$, $x_1 = 0$
$P_2 = 100$ kPa

$T_{r1} = T_{r2} = 313.2/456.9 = 0.685$, $P_{r2} = 0.1/3.67 = 0.027$

From Fig. D.2: $P_{r1} = 0.084$, $(h^* - h)_1/RT_C = 4.9$

From D.1: saturated $P_1 = 0.084 \times 3670 = 308$ kPa

$P_2 < P_1$ with no work done, so process is irreversibel.

Energy Eq.: $q + h_1 = h_2$, Entropy Eq.: $s_1 + \int dq/T + s_{gen} = s_2$, $s_{gen} > 0$

From Fig. D.2: $(h^* - h)_2/RT_C = 0.056$

$q = h_2 - h_1 = 8.3145 \times 456.9 \left[-0.056 + 0 + 4.90\right]/152.93 = \mathbf{120.4\ kJ/kg}$

13.72

An ordinary lighter is nearly full of liquid propane with a small amount of vapor, the volume is 5 cm^3, and temperature is 23°C. The propane is now discharged slowly such that heat transfer keeps the propane and valve flow at 23°C. Find the initial pressure and mass of propane and the total heat transfer to empty the lighter.

Propane C_3H_8 $\quad T_1 = 23^oC = 296.2\text{ K} = \text{constant}, \quad x_1 = 0.0$

$V_1 = 5\text{ cm}^3 = 5\times10^{-6}\text{ m}^3, \quad T_{r1} = 296.2/369.8 = 0.804$

From Figs. D.1 and D.2,

$P_1 = P_{G\,T1} = 0.25\times4.25 = 1.063\text{ MPa}, \quad Z_1 = 0.04$

$(h_1^*-h_1) = 0.188\ 55\times369.8\times4.51 = 314.5$

$$m_1 = \frac{P_1V_1}{Z_1RT_1} = \frac{1063\times5\times10^{-6}}{0.04\times0.188\ 55\times296.2} = 0.00238\text{ kg}$$

State 2: Assume vapor at 100 kPa, 23°C

Therefore, m_2 much smaller than m_1 (~ 9.0×10^{-6} kg)

$$\begin{aligned} Q_{CV} &= m_2u_2 - m_1u_1 + m_eh_e \\ &= m_2h_2 - m_1h_1 - (P_2-P_1)V + (m_1-m_2)h_e \\ &= m_2(h_2-h_e) + m_1(h_e-h_1) - (P_2-P_1)V \end{aligned}$$

$(h_e - h_1) = 0 + 0 + 314.5$

$Q_{CV} = \approx 0 + 0.00238(314.5) - (100-1063)\times5\times10^{-6} = \mathbf{0.753\ kJ}$

Actual lighters uses butane and some propane.

13.73

A piston/cylinder contains 5 kg of butane gas at 500 K, 5 MPa. The butane expands in a reversible polytropic process to 3 MPa, 460 K. Determine the polytropic exponent n and the work done during the process.

C_4H_{10} m = 5 kg $T_1 = 500$ K $P_1 = 5$ MPa

Rev. polytropic process: $P_1V_1^n = P_2V_2^n$

$$T_{r1} = \frac{500}{425.2} = 1.176, \quad P_{r1} = \frac{5}{3.8} = 1.316 \quad \text{From Fig. D.1:} \quad Z_1 = 0.68$$

$$T_{r2} = \frac{460}{425.2} = 1.082, \quad P_{r2} = \frac{3}{3.8} = 0.789 \quad \text{From Fig. D.1:} \quad Z_2 = 0.74$$

$$V_1 = \frac{mZRT}{P} = \frac{5 \times 0.68 \times 0.1430 \times 500}{5000} = 0.0486 \text{ m}^3$$

$$V_2 = \frac{mZRT}{P} = \frac{5 \times 0.74 \times 0.1430 \times 460}{3000} = 0.0811 \text{ m}^3$$

Solve for the polytropic exponent, n, as

$$n = \ln(P_1/P_2) \,/\, \ln(V_2/V_1) = \ln\left(\frac{5}{3}\right) / \ln\left(\frac{0.0811}{0.0486}\right) = \mathbf{0.9976}$$

$${}_1W_2 = \int_1^2 PdV = \frac{P_2V_2 - P_1V_1}{1-n} = \frac{3000\times0.0811 - 5000\times0.0486}{1 - 0.9976} = \mathbf{125\ kJ}$$

13.74

Calculate the heat transfer during the process described in Problem 13.73.

From solution **13.73**,

$V_1 = 0.0486\ \text{m}^3,\quad V_2 = 0.0811\ \text{m}^3,\quad {}_1W_2 = 125\ \text{kJ}$

$T_{r1} = \frac{500}{425.2} = 1.176,\quad P_{r1} = \frac{5}{3.8} = 1.316\quad$ From Fig. D.1: $\quad Z_1 = 0.68$

$T_{r2} = 1.082,\ \ P_{r2} = 0.789,\ \ T_2 = 460\ \text{K}$

From Fig. D.2: $\quad (h^* - h)_1 = 1.30\ RT_C\ ,\quad (h^* - h)_2 = 0.90\ RT_C$

$h^*_2 - h^*_1 = 1.716(460 - 500) = -83.1\ \text{kJ/kg}$

$h_2 - h_1 = -83.1 + \frac{8.3145\times 425.2}{58.124}(-0.90 + 1.30) = -58.8\ \text{kJ/kg}$

$U_2 - U_1 = m(h_2 - h_1) - P_2V_2 + P_1V_1$

$= 5(-58.8) - 3000 \times 0.0811 + 5000 \times 0.0486 = -288.3\ \text{kJ}$

${}_1Q_2 = U_2 - U_1 + {}_1W_2 = \mathbf{-174.3\ kJ}$

13.75

A cylinder contains ethylene, C_2H_4, at 1.536 MPa, −13°C. It is now compressed in a reversible isobaric (constant *P*) process to saturated liquid. Find the specific work and heat transfer.

Ethylene C_2H_4 ; $P_1 = 1.536 \text{ MPa} = P_2$, $T_1 = -13^oC = 260.2 \text{ K}$

State 2: saturated liquid, $x_2 = 0.0$

$$T_{r1} = \frac{260.2}{282.4} = 0.921 \quad P_{r1} = P_{r2} = \frac{1.536}{5.04} = 0.305$$

From Figs. D.1, D.2: $Z_1 = 0.85$, $(h^*_1\text{-}h_1)/RT_c = 0.40$

$$v_1 = \frac{Z_1RT_1}{P_1} = \frac{0.85\times0.29637\times260.2}{1536} = 0.042675$$

$(h^*_1\text{-}h_1) = 0.296\,37\times282.4\times0.40 = 33.5$

From Figs. D.1, D.2: $T_2 = 0.824\times282.4 = 232.7 \text{ K}$

$Z_2 = 0.05$, $(h^*_2\text{-}h_2)/RT_c = 4.42$

$$v_2 = \frac{Z_2RT_2}{P_2} = \frac{0.05\times0.29637\times232.7}{1536} = 0.002245$$

$(h^*_2\text{-}h_2) = 0.296\,37\times282.4\times4.42 = 369.9$

$(h^*_2\text{-}h^*_1) = C_{P0}(T_2\text{-}T_1) = 1.5482(232.7\text{-}260.2) = -42.6$

$w_{12} = \int Pdv = P(v_2\text{-}v_1) = 1536(0.002\,245\text{-}0.042\,675) =$ **-62.1 kJ/kg**

$q_{12} = (u_2\text{-}u_1) + w_{12} = (h_2\text{-}h_1) = -369.9 - 42.6 + 33.5 =$ **-379 kJ/kg**

13.76

Carbon dioxide collected from a fermentation process at 5°C, 100 kPa should be brought to 243 K, 4 MPa in a steady flow process. Find the minimum amount of work required and the heat transfer. What devices are needed to accomplish this change of state?

$$T_{ri} = \frac{278.2}{304.1} = 0.915, \quad P_{ri} = \frac{100}{7380} = 0.0136$$

From D.2 and D.3 : $(h^*\text{-}h)_{ri}/RT_C = 0.02, \quad (s^*\text{-}s)_{ri}/R = 0.01$

$$T_{re} = \frac{243}{304.1} = 0.80, \quad P_{re} = \frac{4}{7.38} = 0.542$$

From D.2 and D.3: $(h^*\text{-}h)_{re}/RT_C = 4.5$, $(s^*\text{-}s)_{re}/R = 4.74$

$$(h_i\text{-}h_e) = -\,(h_i^*\text{-}h_i) + (h_i^*\text{-}h_e^*) + (h_e^*\text{-}h_e)$$

$$= -\,0.188\,92\times304.1\times0.01 + 0.8418(278.2\text{-}243)$$

$$+\,0.188\,92\times304.1\times4.5 \quad = 287.6\text{ kJ/kg}$$

$$(s_i\text{-}s_e) = -\,(s_i^*\text{-}s_i) + (s_i^*\text{-}s_e^*) + (s_e^*\text{-}s_e)$$

$$= -\,0.188\,92\times0.01 + 0.8418\ln(278.2/243)$$

$$-\,0.188\,92\ln(0.1/4) + 0.188\,92\times4.74 \;= 1.7044\text{ kJ/kg K}$$

$$w^{rev} = (h_i\text{-}h_e) - T_0(s_i\text{-}s_e) \;= 287.6 - 278.2(1.7044) = \mathbf{-186.6\ kJ/kg}$$

$$q^{rev} = (h_e\text{-}h_i) + w^{rev} \;= -287.6 - 186.6 = \mathbf{-474.2\ kJ/kg}$$

We need a compressor to bring the pressure up and a cooler to bring the temperature down. Cooling it before compression and intercooling between stages in the compressor lowers the compressor work. In an actual set-up we require more work than the above reversible limit.

13.77

Consider the following equation of state, expressed in terms of reduced pressure and temperature:

$$Z = 1 + \frac{P_r}{14\ T_r}\left(1 - \frac{6}{T_r^2}\right)$$

What does this equation predict for enthalpy departure from the ideal gas value at the state $P_r = 0.4$, $T_r = 0.9$?

$$Z = \frac{Pv}{RT} = 1 + \frac{P_r}{14\ T_r}\left(1 - \frac{6}{T_r^2}\right)$$

$$v = \frac{RT}{P} + \frac{RT_c}{14P_c}\left(1 - \frac{6T_c^2}{T^2}\right) ; \quad \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P} + \frac{12RT_c^3}{14P_cT^3}$$

$$v - T\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT_c}{14P_c} - \frac{18RT_c^3}{14P_cT^2}$$

Now Eq.13.27 is integrated with limits similar to Eq.13.62

$$h - h^* = \int_0^P \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dP = \frac{RT_c}{14}\left(1 - \frac{18}{T_r^2}\right) P_r = \mathbf{0.606\ RT_c}$$

13.78

Consider the following equation of state, expressed in terms of reduced pressure and temperature:

$$Z = 1 + \frac{P_r}{14\ T_r}\left(1 - \frac{6}{T_r^2}\right)$$

What does this equation predict for entropy departure from the ideal gas value at the state $P_r = 0.4$, $T_r = 0.9$?

The entropy departure is the change in s for a real gas minus the change in s for an ideal gas, so from Eq.13.32 and eq.8.23 we get

$$d(s - s^*) = C_p\frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_p dP - \left[\ C_p\frac{dT}{T} - \frac{R}{P}\,dP\right] = \left[\frac{R}{P} - \left(\frac{\partial v}{\partial T}\right)_p\right] dP$$

Solve now for v from the compressibility factor (Z = Pv/RT) to get

$$Z = \frac{Pv}{RT} = 1 + \frac{P_r}{14\ T_r}\left(1 - \frac{6}{T_r^2}\right)$$

$$v = \frac{RT}{P} + \frac{RT_c}{14P_c}\left(1 - \frac{6T_c^2}{T^2}\right) ; \quad \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P} + \frac{12RT_c^3}{14P_cT^3}$$

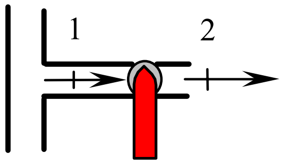
$$s - s^* = \int_0^P \left[\frac{R}{P} - \left(\frac{\partial v}{\partial T}\right)_p\right] dP = \int_0^P \left[- \frac{12RT_c^3}{14P_cT^3}\right] dP = -\frac{6}{7}R\frac{P_r}{T_r^3}$$

Evaluate at $P_r = 0.4$, $T_r = 0.9$ to get

$s - s^* = \mathbf{-0.4703\ R}$

13.79

A flow of oxygen at 230 K, 5 MPa is throttled to 100 kPa in a steady flow process. Find the exit temperature and the entropy generation.



Process: Throttling
Small surface area: $\dot{Q} = 0$;
No shaft: $\dot{W} = 0$
Irreversible: $\dot{S}_{gen} > 0$

We will soove the problem using generalized charts.

$$T_{ri} = \frac{230}{154.6} = 1.488, \quad P_{ri} = \frac{5}{5.04} = 0.992, \quad P_{re} = \frac{0.1}{5.04} = 0.02$$

From D.2: $(h^*_i - h_i) = 0.2598 \times 154.6 \times 0.50 = 20.1$

Energy Eq.: $(h_e - h_i) = 0 = -(h^*_e - h_e) + (h^*_e - h^*_i) + (h^*_i - h_i)$

Assume $T_e = 208$ K , $T_{re} = 1.345$: $(h^*_e - h^*_i) = 0.922(208 - 230) = -20.3$

From D.2: $(h^*_e - h_e) = 0.2598 \times 154.6 \times 0.01 = 0.4$

Check first law $(h_e - h_i) = -0.4 -20.3 + 20.1 \approx 0$ OK => $T_e = \mathbf{208\ K}$

From D.3,

$(s^*_i - s_i) = 0.2598 \times 0.25 = 0.0649$ and $(s^*_e - s_e) = 0.2598 \times 0.01 = 0.0026$

$$(s^*_e - s^*_i) = 0.9216 \ln \frac{208}{230} - 0.2598 \ln \frac{0.1}{5} = 0.9238 \text{ kJ/kg K}$$

$s_{gen} = (s_e - s_i) = -0.0026 + 0.9238 + 0.0649 =$ **0.9861 kJ/kg K**

13.80

A cylinder contains ethylene, C_2H_4, at 1.536 MPa, −13°C. It is now compressed isothermally in a reversible process to 5.12 MPa. Find the specific work and heat transfer.

Ethylene C_2H_4 $P_1 = 1.536$ MPa , $T_2 = T_1 = -13^oC = 260.2$ K

$T_{r2} = T_{r1} = 260.2 / 282.4 = 0.921$, $P_{r1} = 1.536 / 5.04 = 0.305$

From D.1, D.2 and D.3: $Z_1 = 0.85$

$(h^*_1 - h_1) = 0.2964 \times 282.4 \times 0.40 = 33.5$ and $(s^*_1 - s_1) = 0.2964 \times 0.30 = 0.0889$

From D.1, D.2 and D.3: $Z_2 = 0.17$, $P_{r2} = 5.12/5.04 = 1.016$ (comp. liquid)

$(h^*_2 - h_2) = 0.2964 \times 282.4 \times 4.0 = 334.8$ and $(s^*_2 - s_2) = 0.2964 \times 3.6 = 1.067$

Ideal gas: $(h^*_2 - h^*_1) = 0$ and $(s^*_2 - s^*_1) = 0 - 0.2964 \ln \frac{5.12}{1.536} = -0.3568$

${}_1q_2 = T(s_2 - s_1) = 260.2(-1.067 - 0.3568 + 0.0889) =$ **-347.3 kJ/kg**

$(h_2 - h_1) = -334.8 + 0 + 33.5 = -301.3$ kJ/kg

$(u_2 - u_1) = (h_2 - h_1) - RT(Z_2 - Z_1) = -301.3 - 0.2964 \times 260.2(0.17 - 0.85) = -248.9$

${}_1w_2 = {}_1q_2 - (u_2 - u_1) = -347.3 + 248.9 =$ **-98.4 kJ/kg**

13.81

Saturated vapor R-22 at 30°C is throttled to 200 kPa in a steady flow process. Calculate the exit temperature assuming no changes in the kinetic energy, using the generalized charts, Fig. D.2 and the R-22 tables, Table B.4.

R-22 throttling process 1st law: $h_2-h_1 = (h_2-h_2^*) + (h_2^*-h_1^*) + (h_1^*-h_1) = 0$

a) Generalized Chart, Fig. D.2, $R = 8.31451/86.469 = 0.096156$

$$T_{r1} = \frac{303.2}{369.3} = 0.821 \quad => \quad (h_1^*-h_1) = 0.096156 \times 369.3\ (0.53) = 18.82$$

For C_{P0}, use h values from Table B.4 at low pressure.

$C_{P0} \approx 278.115 - 271.594) / (30 - 20) = 0.6521$ kJ/kg K

Substituting: $(h_2-h_2^*) + 0.6521(T_2-30) + 18.82 = 0$

at $P_{r2} = 200/4970 = 0.040$

Assume $T_2 = 5.0\ ^oC$ => $T_{r2} = 278.2/369.3 = 0.753$

$(h_2^*-h_2) = RT \times 0.07 = 0.096156 \times 369.3\ (0.07) = 2.49$

Substituting : $-2.49 + 0.6521(5.0-30) + 18.82 = -0.03 \approx 0$

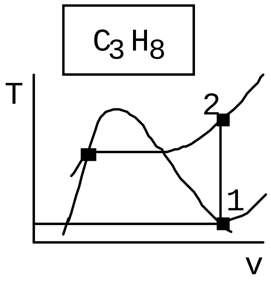
$\Rightarrow T_2$ **= 5.0 °C**

b) R-22 tables, B.4: at $T_1 = 30\ ^oC$, $x_1 = 1.0$ => $h_1 = 259.12$ kJ/kg

$h_2 = h_1 = 259.12$, $P_2 = 0.2$ MPa => $T_2 =$ **4.7 °C**

13.82

250-L tank contains propane at 30°C, 90% quality. The tank is heated to 300°C. Calculate the heat transfer during the process.



$V = 250\text{ L} = 0.25\text{ m}^3$

$T_1 = 30\ ^oC = 303.2\text{ K},\ x_1 = 0.90$

Heat to $T_2 = 300\ ^oC = 573.2\text{ K}$

$M = 44.094,\ T_C = 369.8\text{ K},\ P_C = 4.25\text{ MPa}$

$R = 0.188\ 55,\quad C_{P0} = 1.6794$

$T_{r1} = 0.82 \rightarrow$ Fig. D.1:

$Z_1 = (1 - x_1)\, Z_{f1} + x_1\, Z_{g1} = 0.1 \times 0.05 + 0.9 \times 0.785 = 0.711$

Fig D.2: $\dfrac{h_1^* - h_1}{RT_c} = 0.1 \times 4.43 + 0.9 \times 0.52 = 0.911$

$P_r^{SAT} = 0.30 \quad P_1^{SAT} = 1.275\text{ MPa}$

$$m = \frac{1275 \times 0.25}{0.711 \times 0.188\ 55 \times 303.2} = 7.842\text{ kg}$$

$$P_{r2} = \frac{7.842 \times Z_2 \times 0.188\ 55 \times 573.2}{0.25 \times 4250} = \frac{Z_2}{1.254}$$

at $T_{r2} = 1.55$ Trial and error on P_{r2}

$P_{r2} = 0.743 \Rightarrow P_2 = 3.158\text{ MPa},\quad Z_2 = 0.94\ ,\ (h^* - h)_2 = 0.35\ RT_C$

$(h_2^* - h_1^*) = 1.6794(300-30) \qquad = 453.4\text{ kJ/kg}$

$(h_1^* - h_1) = 0.911 \times 0.188\ 55 \times 369.8 = 63.5\text{ kJ/kg}$

$(h_2^* - h_2) = 0.35 \times 0.188\ 55 \times 369.8 = 24.4\text{ kJ/kg}$

$Q_{12} = m(h_2 - h_1) - (P_2 - P_1)V = 7.842(-24.4+453.4+63.5) - (3158-1275) \times 0.25$

$= +3862 - 471 =$ **3391 kJ**

13.83

The new refrigerant fluid R-123 (see Table A.2) is used in a refrigeration system that operates in the ideal refrigeration cycle, except the compressor is neither reversible nor adiabatic. Saturated vapor at -26.5°C enters the compressor and superheated vapor exits at 65°C. Heat is rejected from the compressor as 1 kW, and the R-123 flow rate is 0.1 kg/s. Saturated liquid exits the condenser at 37.5°C. Specific heat for R-123 is $C_P = 0.6$ kJ/kg. Find the coefficient of performance.

R-123: $T_c = 456.9$ K, $P_c = 3.67$ MPa, M = 152.93 kg/kmol, R = 0.05438 kJ/kg K

State 1: $T_1 = -26.5^oC = 246.7$ K, sat vap., $x_1 = 1.0$

$T_{r1} = 0.54$, Fig D.1, $P_{r1} = 0.01$, $P_1 = P_{r1}P_c = 37$ kPa

Fig. D.2, $h^*_1\text{-}h_1 = 0.03\ RT_C = 0.8$ kJ/kg

State 2: $T_2 = 65^oC = 338.2$ K

State 3: $T_3 = 37.5^oC = 310.7$ K, sat. liq., $x_3 = 0$

$T_{r3} = 0.68$, Fig. D.1: $P_{r3} = 0.08$, $P_3 = P_{r3}P_c = 294$ kPa

$P_2 = P_3 = 294$ kPa, $P_{r2} = 0.080$, $T_{r2} = 0.74$,

Fig. D.2: $h^*_2\text{-}h_2 = 0.25\ RT_C = 6.2$ kJ/kg

$h^*_3\text{-}h_3 = 4.92\ RT_C = 122.2$ kJ/kg

State 4: $T_4 = T_1 = 246.7$ K, $h_4 = h_3$

1st Law Evaporator: $q_L + h_4 = h_1 + w$; $w = 0$, $h_4 = h_3$

$$q_L = h_1 - h_3 = (h_1 - h^*_1) + (h^*_1 - h^*_3) + (h^*_3 - h_3)$$

$h^*_1 - h^*_3 = C_P(T_1 - T_3) = -38.4$ kJ/kg, $q_L = -0.8 - 38.4 + 122.2 = 83.0$ kJ/kg

1st Law Compressor: $q + h_1 = h_2 + w_c$; $\dot{Q} = -1.0$ kW, $\dot{m} = 0.1$ kg/s

$$w_c = h_1 - h_2 + q;\ h_1 - h_2 = (h_1 - h^*_1) + (h^*_1 - h^*_2) + (h^*_2 - h_2)$$

$h^*_1 - h^*_2 = C_P(T_1 - T_2) = -54.9$ kJ/kg,

$w_c = -0.8 - 54.9 + 6.2 - 10.0 = -59.5$ kJ/kg

$\beta = q_L/w_c = 83.0/59.5 =$ **1.395**

13.84

An uninsulated piston/cylinder contains propene, C_3H_6, at ambient temperature, 19°C, with a quality of 50% and a volume of 10 L. The propene now expands very slowly until the pressure in the cylinder drops to 460 kPa. Calculate the mass of propene, the work, and heat transfer for this process.

Propene C_3H_6: $T_1 = 19^oC = 292.2$ K, $x_1 = 0.50$, $V_1 = 10$ L

From Fig. D.1: $T_{r1} = 292.2/364.9 = 0.80$,

$P_{r1} = P_{r\ sat} = 0.25$, $P_1 = 0.25 \times 4.6 = 1.15$ MPa

From D.1: $Z_1 = 0.5 \times 0.04 + 0.5 \times 0.805 = 0.4225$

$$m = \frac{P_1V_1}{Z_1RT_1} = \frac{1150\times0.010}{0.4225\times0.197\ 58\times292.2} = \mathbf{0.471\ kg}$$

Assume reversible and isothermal process (slow, no friction, not insulated)

$${}_1Q_2 = m(u_2-u_1) + {}_1W_2$$

$${}_1W_2 = \int_1^2 PdV \text{ (cannot integrate)}; \qquad {}_1Q_2 = \int_1^2 TdS = Tm(s_2-s_1)$$

From Figs. D.2 and D.3:

$$h^*_1 - h_1 = 0.19758 \times 364.9(0.5 \times 4.51 + 0.5 \times 0.46) = 179.2 \text{ kJ/kg}$$

$$(s^*_1 - s_1) = 0.197\ 58\ (0.5 \times 5.46 + 0.5 \times 0.39) = 0.5779 \text{ kJ/kg K}$$

The ideal gas change in h and s are

$$(h^*_2 - h^*_1) = 0 \text{ and } \quad (s^*_2 - s^*_1) = 0 - 0.197\ 58 \ln\frac{460}{1161} = +\ 0.1829 \text{ kJ/kg K}$$

At $T_{r2} = 0.80$, $P_{r2} = 0.10$, from D.1, D.2 and D.3, $Z_2 = 0.93$

$$(h^*_2 - h_2) = 0.197\ 58 \times 364.9 \times 0.16 = 11.5 \text{ kJ/kg}$$

$$(s^*_2 - s_2) = 0.197\ 58 \times 0.13 = 0.0257 \text{ kJ/kg K}$$

Now we can do the change in s and h from state 1 to state 2

$$(s_2 - s_1) = -(s^*_2 - s_2) + (s^*_2 - s^*_1) + (s^*_1 - s_1)$$
$$= -0.0257 + 0.1829 + 0.5779 = 0.7351 \text{ kJ/kg K}$$

$$(h_2 - h_1) = -(h^*_2 - h_2) + (h^*_2 - h^*_1) + h^*_1 - h_1$$
$$= -11.5 + 0 + 179.2 = 167.7 \text{ kJ/kg}$$

The heat transfer is found from the second law

$_1q_2 = 292.2 \times 0.7351 = 214.8$ kJ/kg => $_1Q_2 = m\ _1q_2 = \mathbf{101.2\ kJ}$

We need the internal energy in the energy equation

$$u_2 - u_1 = (h_2 - h_1) + RT(Z_1 - Z_2) = 167.7 + 0.197\,58 \times 292.2\ (0.4225 - 0.93)$$

$$= 138.4 \text{ kJ/kg}$$

$$_1w_2 = {_1q_2} - (u_2 - u_1) = 214.8 - 138.4 = 76.4 \text{ kJ/kg}$$

$$_1W_2 = m\ _1w_2 = \mathbf{36.0\ kJ}$$

13.85

A geothermal power plant on the Raft River uses isobutane as the working fluid. The fluid enters the reversible adiabatic turbine, as shown in Fig. P13.42, at 160°C, 5.475 MPa, and the condenser exit condition is saturated liquid at 33°C. Isobutane has the properties T_c= 408.14 K, P_c= 3.65 MPa, C_{P0}= 1.664 kJ/kg K and ratio of specific heats *k* = 1.094 with a molecular weight as 58.124. Find the specific turbine work and the specific pump work.

Turbine inlet: $T_1 = 160^oC$, $P_1 = 5.475$ MPa

Condenser exit: $T_3 = 33^oC$, $x_3 = 0.0$, $T_{r3} = 306.2 / 408.1 = 0.75$

From Fig. D.1:

$P_{r3} = 0.16$, $Z_3 = 0.03$ => $P_2 = P_3 = 0.16 \times 3.65 = 0.584$ MPa

$T_{r1} = 433.2 / 408.1 = 1.061$, $P_{r1} = 5.475 / 3.65 = 1.50$

From Fig. D.2 & D.3:

$$(h_1^*\text{-}h_1) = 0.143\ 05\times408.1\times2.84 = 165.8$$

$$(s_1^*\text{-}s_1) = 0.143\ 05\times2.15 = 0.3076$$

$$(s_2^*\text{-}s_1^*) = 1.664 \ln\frac{306.2}{433.2} - 0.143\ 05 \ln\frac{0.584}{5.475} = -0.2572$$

$$(s_2^*\text{-}s_2) = (s_2^*\text{-}s_{F2}) - x_2 s_{FG2}$$

$$= 0.143\ 05\times6.12 - x_2\times0.143\ 05(6.12\text{-}0.29) = 0.8755 - x_2\times0.8340$$

$$(s_2\text{-}s_1) = 0 = -0.8755 + x_2\times0.8340 - 0.2572 + 0.3076 \quad => \quad x_2 = 0.99$$

$$(h_2^*\text{-}h_1^*) = C_{P0}(T_2\text{-}T_1) = 1.664(306.2 - 433.2) = -211.3$$

From Fig. D.2:,

$$(h_2^*\text{-}h_2) = (h_2^*\text{-}h_{F2}) - x_2 h_{FG2} = 0.143\ 05\times408.1[4.69\text{-}0.99(4.69\text{-}0.32)]$$

$$= 273.8 - 0.99 \times 255.1 = 21.3$$

Turbine: $w_T = (h_1\text{-}h_2) = -165.8 + 211.3 + 21.3 =$ **66.8 kJ/kg**

Pump: $$v_{F3} = \frac{Z_{F3}RT_3}{P_3} = \frac{0.03\times0.143\ 05\times306.2}{584} = 0.00225$$

$w_P = - \int v\, dP \approx v_{F3}(P_4 - P_3) = -0.00225\ (5475\text{-}584) =$ **-11.0 kJ/kg**

13.86

A line with a steady supply of octane, C_8H_{18}, is at 400°C, 3 MPa. What is your best estimate for the availability in a steady flow setup where changes in potential and kinetic energies may be neglected?

Availability of Octane at $T_i = 400\ ^oC$, $P_i = 3$ MPa

$$P_{ri} = \frac{3}{2.49} = 1.205, \quad T_{ri} = \frac{673.2}{568.8} = 1.184$$

From D.2 and D.3,

$$(h_1^*-h_1) = 0.072\ 79\times568.8\times1.13 = 46.8\ ; \quad (s_1^*-s_1) = 0.072\ 79\times0.69 = 0.05$$

Exit state in equilibrium with the surroundings, assume $T_0 = 298.2$ K, $P_0 =$ 100 kPa

$$T_{r0} = \frac{298.2}{568.8} = 0.524\ , \ P_{r0} = \frac{0.1}{2.49} = 0.040$$

From D.2 and D.3,

$$(h_0^*-h_0) = RT_C\times5.4 = 223.6 \qquad \text{and} \qquad (s_0^*-s_0) = R\times10.37 = 0.755$$

$$(h_i^*-h_0^*) = 1.7113(673.2-298.2) = 641.7$$

$$(s_i^*-s_0^*) = 1.7113 \ln\frac{673.2}{298.2} - 0.072\ 79 \ln\frac{3}{0.1} = 1.1459$$

$$(h_i-h_0) = -46.8 + 641.7 + 223.6 = 818.5$$

$$(s_i-s_0) = -0.05 + 1.1459 + 0.755 = 1.8509$$

$$\varphi_i = w^{rev} = (h_i-h_0) - T_0(s_i-s_0) = 818.5 - 298.2(1.8509) = \mathbf{266.6\ kJ/kg}$$

13.87

An insulated cylinder fitted with a frictionless piston contains saturated-vapor carbon dioxide at 0^oC, at which point the cylinder volume is 20 L. The external force on the piston is now slowly decreased, allowing the carbon dioxide to expand until the temperature reaches - 30^oC. Calculate the work done by the CO_2 during this process.

CO_2: $T_c = 304.1$ K, $P_c = 7.38$ MPa, $C_p = 0.842$ kJ/kg-K, R = 0.1889 kJ/kg K

State 1: $T_1 = 0^oC$, sat. vap., $x_1 = 1.0$, $V_1 = 20$ L

$T_{r1} = 0.9$, $P_1 = P_{r1}P_c = 0.53 \times 7380 = 3911$ kPa, $Z_1 = Z_g = 0.67$

$\left(h^*_1 - h_1\right)_g = 0.9\ RT_C$, $\left(s^*_1 - s_1\right)_g/R = 0.72$, $m = \dfrac{P_1V_1}{Z_1RT_1} = 2.262$ kg

State 2: $T_2 = -30^oC$

$T_{r2} = 0.8$, $P_2 = P_{r2}P_c = 0.25 \times 7380 = 1845$ kPa

2^{nd} Law: $\Delta S_{net} = m(s_2 - s_1) - {}_1Q_2/T$; ${}_1Q_2 = 0$, $\Delta S_{net} = 0$

$$s_2 - s_1 = \left(s_2 - s^*_2\right) + \left(s^*_2 - s^*_1\right) + \left(s^*_1 - s_1\right) = 0$$

$s^*_2 - s^*_1 = C_P \ln\dfrac{T_2}{T_1} - R \ln\dfrac{P_2}{P_1} = 0.044$ kJ/kg-K, $s^*_1 - s_1 = 0.136$ kJ/kg-K

$s^*_2 - s_2 = 0.180$ kJ/kg K, $\left(s^*_2 - s_2\right)_f = 5.46\ R$, $\left(s^*_2 - s_2\right)_g = 0.39\ R$

$\left(s^*_2 - s_2\right) = (1-x_2)\left(s^*_2 - s_2\right)_f + x_2\left(s^*_2 - s_2\right)_g \rightarrow x_2 = 0.889$

1^{st} Law: ${}_1Q_2 = m(u_2 - u_1) + {}_1W_2$; ${}_1Q_2 = 0$, $u = h - Pv$

$Z_2 = (1 - x_2)Z_f + x_2Z_g = 0.111 \times 0.04 + 0.889 \times 0.81 = 0.725$;

$$(h_2 - h_1) = \left(h_2 - h^*_2\right) + \left(h^*_2 - h^*_1\right) + \left(h^*_1 - h_1\right)$$

$h^*_2 - h^*_1 = C_p(T_2 - T_1) = -25.3$ kJ/kg, $\left(h^*_1 - h_1\right) = 51.7$ kJ/kg

$\left(h^*_2 - h_2\right)_f = 4.51\ RT_C$, $\left(h^*_2 - h_2\right)_g = 0.46\ RT_C$

$\left(h^*_2 - h_2\right) = (1 - x_2)\left(h^*_2 - h_2\right)_f + x_2\left(h^*_2 - h_2\right)_g = 52.2$ kJ/kg

$h_2 - h_1 = -52.2 - 25.3 + 51.7 = -25.8$ kJ/kg

$u_2 - u_1 = (h_2 - h_1) - Z_2RT_2 + Z_1RT_1 = -25.8 - 0.725 \times 0.18892 \times 243.2$
$+ 0.67 \times 0.18892 \times 273.2 = -24.5$ kJ/kg

${}_1W_2 = \mathbf{55.4\ kJ}$

13.88

An evacuated 100-L rigid tank is connected to a line flowing R-142b gas, chlorodifluoroethane, at 2 MPa, 100°C. The valve is opened, allowing the gas to flow into the tank for a period of time, and then it is closed. Eventually, the tank cools to ambient temperature, 20°C, at which point it contains 50% liquid, 50% vapor, by volume. Calculate the quality at the final state and the heat transfer for the process. The ideal-gas specific heat of R-142b is $C_p = 0.787$ kJ/kg K.

Rigid tank $V = 100$ L, $m_1 = 0$ Line: R-142b CH_3CClF_2

$M = 100.495$, $T_C = 410.3$ K, $P_C = 4.25$ MPa, $C_{P0} = 0.787$ kJ/kg K

$R = \bar{R}/M = 8.31451 / 100.495 = 0.082\ 73$ kJ/kg K

Line $P_i = 2$ MPa, $T_i = 100\ ^oC$, Flow in to $T_2 = T_0 = 20^oC$

$V_{LIQ\ 2} = V_{VAP\ 2} = 50$ L

Continuity: $m_i = m_2$; Energy: $Q_{CV} + m_i h_i = m_2 u_2 = m_2 h_2 - P_2 V$

From D.2 at i: $P_{ri} = 2 / 4.25 = 0.471$, $T_{ri} = 373.15 / 410.3 = 0.91$

$(h_i^* - h_i) = 0.082\ 73 \times 410.3 \times 0.72 = 24.4$

$(h_2^* - h_i^*) = C_{P0}(T_2 - T_i) = 0.787(20-100) = -63.0$

From D.2: $T_{r2} = \dfrac{293.2}{410.3} = 0.715$ => $P_2 = 0.115 \times 4250 = 489$ kPa

sat. liq.: $Z_F = 0.02$, $(h^* - h_F) = RT_C \times 4.85 = 164.6$

sat. vap.: $Z_G = 0.88$, $(h^* - h_G) = RT_C \times 0.25 = 8.5$

$$m_{LIQ\ 2} = \frac{P_2 V_{LIQ\ 2}}{Z_F R T_2} = \frac{489 \times 0.050}{0.02 \times 0.082\ 73 \times 293.2} = 50.4 \text{ kg}$$

$$m_{VAP\ 2} = \frac{P_2 V_{VAP\ 2}}{Z_G R T_2} = 1.15 \text{ kg}, \qquad m_2 = 51.55 \text{ kg}$$

$x_2 = m_{VAP\ 2}/m_2 = 0.0223$

$(h_2^* - h_2) = (1 - x_2)(h_2^* - h_{F2}) + x_2(h_2^* - h_{G2}) = 0.9777 \times 164.6 + 0.0223 \times 8.5 = 161.1$

$Q_{CV} = m_2(h_2 - h_i) - P_2 V = 51.55(-161.1 - 63.0 + 24.4) - 489 \times 0.10$

$= \mathbf{-10\ 343\ kJ}$

13.89

Saturated liquid ethane at 2.44 MPa enters a heat exchanger and is brought to 611 K at constant pressure, after which it enters a reversible adiabatic turbine where it expands to 100 kPa. Find the heat transfer in the heat exchanger, the turbine exit temperature and turbine work.

From D.2,

$P_{r1} = 2.44/4.88 = 0.50$, $T_{r1} = 0.89$, $T_1 = 0.89 \times 305.4 = 271.8$ K

$(h^*_1 - h_1) = 0.2765 \times 305.4 \times 4.12 = 347.9$

$(h^*_2 - h^*_1) = 1.766\ (611 - 271.8) = 599.0$

$P_{r2} = 0.50$, $T_{r2} = 611/305.4 = 2.00$

From D.2: $(h^*_2 - h_2) = RT_c \times 0.14 = 0.2765 \times 305.4 \times 0.14 = 11.8$

$q = (h_2 - h_1) = -11.8 + 599.0 + 347.9 =$ **935.1 kJ/kg**

From D.3,

$(s^*_2 - s_2) = 0.2765 \times 0.05 = 0.0138$

$$(s^*_3 - s^*_2) = 1.766 \ln \frac{T_3}{611} - 0.2765 \ln \frac{100}{2440}$$

Assume $T_3 = 368$ K , $T_{r3} = 1.205$

at $P_{r3} = 0.020$

$(s^*_3 - s^*_2) = -0.8954 + 0.8833 = -0.0121$

From D.3,

$(s^*_3 - s_3) = 0.2765 \times 0.01 = 0.0028$

$(s_3 - s_2) = -0.0028 - 0.0121 + 0.0138 \approx 0$ OK

Therefore, $T_3 =$ **368 K**

From D.2,

$(h^*_3 - h_3) = 0.2765 \times 305.4 \times 0.01 = 0.8$

$w = (h_2 - h_3) = -11.8 + 1.766\ (611 - 368) + 0.8 =$ **418.1 kJ/kg**

13.90

A control mass of 10 kg butane gas initially at 80°C, 500 kPa, is compressed in a reversible isothermal process to one-fifth of its initial volume. What is the heat transfer in the process?

Butane C_4H_{10}: $m = 10$ kg, $T_1 = 80\ ^oC$, $P_1 = 500$ kPa

Compressed, reversible T = const, to $V_2 = V_1/5$

$$T_{r1} = \frac{353.2}{425.2} = 0.831,\ P_{r1} = \frac{500}{3800} = 0.132$$

From D.1 and D.3: $Z_1 = 0.92$, $(s^*_1 - s_1) = 0.143 \times 0.16 = 0.0230$

$$v_1 = \frac{Z_1RT_1}{P_1} = \frac{0.92 \times 0.143 \times 353.2}{500} = 0.09296\ m^3/kg$$

$v_2 = v_1/5 = 0.01859\ m^3/kg$

At $T_{r2} = T_{r1} = 0.831$

From D.1: $P_G = 0.325 \times 3800 = 1235$ kPa

sat. liq.: $Z_F = 0.05$, $(s^*-s_F) = R \times 5.08 = 0.7266$

sat. vap.: $Z_G = 0.775$, $(s^*-s_G) = R \times 0.475 = 0.0680$

Therefore

$$v_F = \frac{0.05 \times 0.143 \times 353.2}{1235} = 0.00205\ m^3/kg$$

$$v_G = \frac{0.775 \times 0.143 \times 353.2}{1235} = 0.0317\ m^3/kg$$

Since $v_F < v_2 < v_G \rightarrow x_2 = (v_2-v_F)/(v_G-v_F) = 0.5578$

$$(s^*_2 - s_2) = (1 - x_2)(s^*_2 - s_{F2}) + x_2(s^*_2 - s_{G2})$$
$$= 0.4422 \times 0.7266 + 0.5578 \times 0.0680 = 0.3592\ kJ/kg\ K$$

$(s^*_2 - s^*_1) = C_{P0} \ln (T_2/T_1) - R \ln (P_2/P_1) = 0 - 0.143 \ln (1235/500) = -0.1293$

$(s_2 - s_1) = -0.3592 - 0.1293 + 0.0230 = -0.4655$ kJ/kg K

${}_1Q_2 = Tm(s_2 - s_1) = 353.2 \times 10 (-0.4655) = \mathbf{-1644\ kJ}$

13.91

An uninsulated compressor delivers ethylene, C_2H_4, to a pipe, *D* = 10 cm, at 10.24 MPa, 94°C and velocity 30 m/s. The ethylene enters the compressor at 6.4 MPa, 20.5°C and the work input required is 300 kJ/kg. Find the mass flow rate, the total heat transfer and entropy generation, assuming the surroundings are at 25°C.

$$T_{ri} = \frac{293.7}{282.4} = 1.040\ ,\ P_{ri} = \frac{6.4}{5.04} = 1.270$$

From D.2 and D.3,

$$(h_i^* - h_i) = 0.296\,37 \times 282.4 \times 2.65 = 221.8 \text{ kJ/kg}$$

$$(s_i^* - s_i) = 0.296\,37 \times 2.08 = 0.6164 \text{ kJ/kg K}$$

$$T_{re} = \frac{367.2}{282.4} = 1.30\ ,\ P_{re} = \frac{10.24}{5.04} = 2.032 \quad \Rightarrow \text{ From D.1:} \quad Z_e = 0.69$$

$$v_e = \frac{Z_e R T_e}{P_e} = \frac{0.69 \times 0.296\,37 \times 367.2}{10\,240} = 0.0073 \text{ m}^3\text{/kg}$$

$$A_e = \frac{\pi}{4} D_e^2 = 0.007\,85 \text{ m}^2 \quad \Rightarrow \quad \dot{m} = \frac{A_e \mathbf{V}_e}{v_e} = \frac{0.007\,85 \times 30}{0.0073} = \mathbf{32.26\ kg/s}$$

From D.2 and D.3,

$$(h_e^* - h_e) = 0.296\,37 \times 282.4 \times 1.6 = 133.9 \text{ kJ/kg}$$

$$(s_e^* - s_e) = 0.296\,37 \times 0.90 = 0.2667 \text{ kJ/kg K}$$

$$(h_e^* - h_i^*) = 1.5482(367.2 - 293.7) = 113.8$$

$$(s_e^* - s_i^*) = 1.5482 \ln \frac{367.2}{293.7} - 0.296\,37 \ln \frac{10.24}{6.4} = 0.2065$$

$$(h_e - h_i) = -133.9 + 113.8 + 221.8 = 201.7 \text{ kJ/kg}$$

$$(s_e - s_i) = -0.2667 + 0.2065 + 0.6164 = 0.5562 \text{ kJ/kg K}$$

First law:

$$q = (h_e - h_i) + KE_e + w = 201.7 + \frac{30^2}{2 \times 1000} - 300 = -97.9 \text{ kJ/kg}$$

$$\dot{Q}_{cv} = \dot{m}q = 32.26(-97.9) = \mathbf{-3158\ kW}$$

$$\dot{S}_{gen} = -\frac{\dot{Q}_{cv}}{T_o} + \dot{m}(s_e - s_i) = +\frac{3158}{298.2} + 32.26(0.5562) = \mathbf{28.53\ kW/K}$$

13.92

A distributor of bottled propane, C_3H_8, needs to bring propane from 350 K, 100 kPa to saturated liquid at 290 K in a steady flow process. If this should be accomplished in a reversible setup given the surroundings at 300 K, find the ratio of the volume flow rates $\dot{V}_{in}/\dot{V}_{out}$, the heat transfer and the work involved in the process.

From Table A.2: $T_{ri} = \frac{350}{369.8} = 0.946$, $P_{ri} = \frac{0.1}{4.25} = 0.024$

From D.1, D.2 and D.3,

$Z_i = 0.99$

$(h^*_i - h_i) = 0.1886 \times 369.8 \times 0.03 = 2.1$ kJ/kg

$(s^*_i - s_i) = 0.1886 \times 0.02 = 0.0038$ kJ/kg K

$T_{re} = \frac{290}{369.8} = 0.784$,

From D.1, D.2 and D.3,

$P_{re} = 0.22$, $P_e = 0.22 \times 4.25 = 0.935$ MPa and $Z_e = 0.036$

$(h^*_e - h_e) = 0.1886 \times 369.8 \times 4.57 = 318.6$ kJ/kg

$(s^*_e - s_e) = 0.1886 \times 5.66 = 1.0672$ kJ/kg K

$(h^*_e - h^*_i) = 1.679(290 - 350) = -100.8$ kJ/kg

$(s^*_e - s^*_i) = 1.679 \ln \frac{290}{350} - 0.1886 \ln \frac{0.935}{0.1} = -0.7373$ kJ/kg K

$(h_e - h_i) = -318.6 - 100.8 + 2.1 = -417.3$ kJ/kg

$(s_e - s_i) = -1.0672 - 0.7373 + 0.0038 = -1.8007$ kJ/kg K

$$\frac{\dot{V}_{in}}{\dot{V}_{out}} = \frac{Z_i T_i / P_i}{Z_e T_e / P_e} = \frac{0.99}{0.036} \times \frac{350}{290} \times \frac{0.935}{0.1} = \mathbf{310.3}$$

$w^{rev} = (h_i - h_e) - T_0(s_i - s_e) = 417.3 - 300(1.8007) = \mathbf{-122.9\ kJ/kg}$

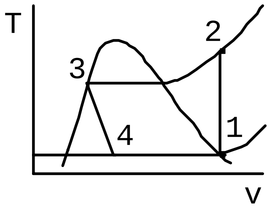
$q^{rev} = (h_e - h_i) + w^{rev} = -417.3 - 122.9 = \mathbf{-540.2\ kJ/kg}$

13.93

The environmentally safe refrigerant R-152a is to be evaluated as the working fluid for a heat pump system that will heat a house. It uses an evaporator temperature of –20°C and a condensing temperature of 30°C. Assume all processes are ideal and R-152a has a heat capacity of $C_p = 0.996$ kJ/kg K. Determine the cycle coefficient of performance.

Ideal Heat Pump $T_H = 30\ ^oC$

From A.2: $M = 66.05$, $R = 0.125\ 88$, $T_C = 386.4$ K, $P_C = 4.52$ MPa



$$T_{r3} = \frac{303.2}{386.4} = 0.785$$

$P_{r3} = P_{r2} = 0.22 \quad => \quad P_3 = P_2 = 994$ kPa

Sat.liq.: $h_3^* - h_3 = 4.56{\times}RT_C = 221.8$

$T_1 = -20\ ^oC = 253.2$ K, $T_{r1} = 0.655$, $P_{r1} = 0.058 \rightarrow P_1 = 262$ kPa

$h_1^* - h_1 = 0.14{\times}RT_C = 6.8$ and $s_1^* - s_1 = 0.14{\times}R = 0.0176$

Assume $T_2 = 307$ K, $T_{r2} = 0.795$ given $P_{r2} = 0.22$

From D.2, D.3: $s_2^* - s_2 = 0.34{\times}R = 0.0428$; $h_2^* - h_2 = 0.40{\times}RT_c = 19.5$

$$s_2^* - s_1^* = 0.996 \ln\frac{307}{253.2} - 0.125\ 88 \ln\frac{994}{262} = 0.0241$$

$s_2 - s_1 = -0.0428 + 0.0241 + 0.0176 = -0.001 \approx 0$ OK

$\Rightarrow h_2 - h_1 = -19.5 + 0.996(307-253.2) + 6.8 = 40.9$

$h_2 - h_3 = -19.5 + 0.996(307-303.2) + 221.8 = 206.1$

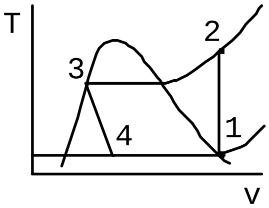
$$\beta = \frac{q_H}{w_{IN}} = \frac{h_2 - h_3}{h_2 - h_1} = \frac{206.1}{40.9} = \mathbf{5.04}$$

13.94

Rework the previous problem using an evaporator temperature of $0^{o}C$.

Ideal Heat Pump $T_H = 30\ ^oC$

From A.2: $M = 66.05,\ R = 0.125\ 88,\ T_C = 386.4\ K,\ P_C = 4.52\ MPa$



$$T_{r3} = \frac{303.2}{386.4} = 0.785$$

$P_{r3} = P_{r2} = 0.22 \quad => \quad P_3 = P_2 = 994$ kPa

Sat.liq.: $h_3^* - h_3 = 4.56 \times RT_C = 221.8$

$T_1 = 0\ ^oC = 273.2$ K, $T_{r1} = 0.707 \ => \ P_{r1} = 0.106,\ P_1 = 479$ kPa

$h_1^* - h_1 = 0.22 \times RT_C = 10.7$ and $s_1^* - s_1 = 0.21 \times R = 0.0264$

Assume $T_2 = 305$ K, $T_{r2} = 0.789$

$s_2^* - s_2 = 0.35 \times R = 0.0441$ and $h_2^* - h_2 = 0.38 \times RT_C = 18.5$

$$s_2^* - s_1^* = 0.996 \ln\frac{305.0}{273.2} - 0.125\ 88 \ln\frac{994}{479} = 0.0178$$

$s_2 - s_1 = -0.0441 + 0.0178 + 0.0264 = 0.0001 \approx 0$ OK

$h_2 - h_1 = -18.5 + 0.996(305.0-273.2) + 10.7 = 23.9$

$h_2 - h_3 = -18.5 + 0.996(305.0-303.2) + 221.8 = 205.1$

$$\beta = \frac{h_2 - h_3}{h_2 - h_1} = \frac{205.1}{23.9} = \mathbf{8.58}$$

Mixtures

13.95

A 2 kg mixture of 50% argon and 50% nitrogen by mole is in a tank at 2 MPa, 180 K. How large is the volume using a model of (a) ideal gas and (b) Kays rule with generalized compressibility charts.

a) Ideal gas mixture

Eq.12.5: $M_{mix} = \sum y_i M_i = 0.5 \times 39.948 + 0.5 \times 28.013 = 33.981$

$$V = \frac{m\bar{R}T}{M_{mix}P} = \frac{2 \times 8.3145 \times 180}{33.981 \times 2000} = \mathbf{0.044\ m^3}$$

b) Kay's rule Eq.13.86

$P_{c\ mix} = 0.5 \times 4.87 + 0.5 \times 3.39 = 4.13$ MPa

$T_{c\ mix} = 0.5 \times 150.8 + 0.5 \times 126.2 = 138.5$ K

Reduced properties: $P_r = \frac{2}{4.13} = 0.484, \quad T_r = \frac{180}{138.5} = 1.30$

Fig. D.1: $Z = 0.925$

$$V = Z \frac{m\bar{R}T}{M_{mix}P} = 0.925 \times 0.044 = \mathbf{0.0407\ m^3}$$

13.96

A 2 kg mixture of 50% argon and 50% nitrogen by mass is in a tank at 2 MPa, 180 K. How large is the volume using a model of (a) ideal gas and (b) van der Waals equation of state with a, b for a mixture?

a) Ideal gas mixture

Eq.12.15: $R_{mix} = \sum c_i R_i = 0.5 \times 0.2081 + 0.5 \times 0.2968 = 0.25245$ kJ/kg K

$$V = \frac{mR_{mix}T}{P} = \frac{2 \times 0.25245 \times 180}{2000} = \mathbf{0.0454\ m^3}$$

b) van der Waals equation of state. before we can do the parameters a, b for the mixture we need the individual component parameters.

$$a_{Ar} = \frac{27}{64}\frac{R^2T_c^2}{P_c} = \frac{27}{64}\frac{(0.2081 \times 150.8)^2}{4870} = 0.08531$$

$$a_{N2} = \frac{27}{64}\frac{R^2T_c^2}{P_c} = \frac{27}{64}\frac{(0.2968 \times 126.2)^2}{3390} = 0.17459$$

$$b_{Ar} = \frac{RT_c}{8P_c} = \frac{0.2081 \times 150.8}{8 \times 4870} = 0.000\ 805$$

$$b_{N2} = \frac{RT_c}{8P_c} = \frac{0.2968 \times 126.2}{8 \times 3390} = 0.001\ 381$$

Now the mixture parameters are from eq.13.87

$$a_{mix} = \left(\sum c_i\, a_i^{1/2}\right)^2 = (0.5 \times \sqrt{0.08531} + 0.5 \times \sqrt{0.17459})^2 = 0.126$$

$$b_{mix} = \sum c_i\, b_i = 0.5 \times 0.000\ 805 + 0.5 \times 0.001\ 381 = 0.001\ 093$$

Using now eq.13.52: $$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$2000 = \frac{0.25245 \times 180}{v - 0.001\ 093} - \frac{0.126}{v^2}$$

By trial and error we find the specific volume, $v = 0.02097\ m^3/kg$

$$V = mv = \mathbf{0.04194\ m^3}$$

13.97

A 2 kg mixture of 50% argon and 50% nitrogen by mass is in a tank at 2 MPa, 180 K. How large is the volume using a model of (a) ideal gas and (b) Redlich Kwong equation of state with a, b for a mixture.

a) Ideal gas mixture

Eq.12.15: $R_{mix} = \sum c_i R_i = 0.5 \times 0.2081 + 0.5 \times 0.2968 = 0.25245 \text{ kJ/kg K}$

$$V = \frac{mR_{mix}T}{P} = \frac{2 \times 0.25245 \times 180}{2000} = \mathbf{0.0454\ m^3}$$

b) Redlich Kwong equation of state. Before we can do the parameters a, b for the mixture we need the individual component parameters, Eq.13.58, 13.59.

$$a_{Ar} = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} = 0.42748 \frac{0.2081^2 \times 150.8^{2.5}}{4870} = 1.06154$$

$$a_{N2} = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} = 0.42748 \frac{0.2968^2 \times 126.2^{2.5}}{3390} = 1.98743$$

$$b_{Ar} = 0.08664 \frac{RT_c}{P_c} = 0.08664 \frac{0.2081 \times 150.8}{4870} = 0.000\,558$$

$$b_{N2} = 0.08664 \frac{RT_c}{P_c} = 0.08664 \frac{0.2968 \times 126.2}{3390} = 0.000\,957$$

Now the mixture parameters are from eq.13.87

$$a_{mix} = \left(\sum c_i\, a_i^{1/2}\right)^2 = (0.5 \times \sqrt{1.06154} + 0.5 \times \sqrt{1.98743})^2 = 1.4885$$

$$b_{mix} = \sum c_i\, b_i = 0.5 \times 0.000\,558 + 0.5 \times 0.000\,957 = 0.000\,758$$

Using now eq.13.57: $P = \frac{RT}{v - b} - \frac{a}{v(v + b)T^{1/2}}$

$$2000 = \frac{0.25245 \times 180}{v - 0.000\,758} - \frac{1.4885}{v(v + 0.000\,758)\ 180^{1/2}}$$

By trial and error we find the specific volume, $v = 0.02102 \text{ m}^3\text{/kg}$

$$V = mv = \mathbf{0.04204\ m^3}$$

13.98

Saturated-liquid ethane at T_1 = 14°C is throttled into a steady flow mixing chamber at the rate of 0.25 kmol/s. Argon gas at T_2 = 25°C, P_2 = 800 kPa, enters the chamber at the rate of 0.75 kmol/s. Heat is transferred to the chamber from a heat source at a constant temperature of 150°C at a rate such that a gas mixture exits the chamber at T_3 = 120°C, P_3 = 800 kPa. Find the rate of heat transfer and the rate of entropy generation.

Argon, $T_{a2} = 25^oC$, $P_2 = 800$ kPa, $\dot{n}_2 = 0.75$ kmol/s

$T_{ca} = 150$ K, $P_{ca} = 4.87$ MPa, $M_a = 39.948$ kg/kmol, $C_{pa} = 0.52$ kJ/kg K

$\bar{h}_{a3} - \bar{h}_{a2} = M_aC_{pa}(T_3 - T_{a2}) = 1973.4$ kJ/kmol

Inlet: Ethane, $T_{b1} = 14^oC$, sat. liq., $x_{b1} = 0$, $\dot{n}_1 = 0.25$ kmol/s

$T_{cb} = 305.4$ K, $P_{cb} = 4.88$ MPa, $M_b = 30.07$ kg/kmol, $C_{pb} = 1.766$ kJ/kg-K

$T_{r1} = 0.94$, $P_{b1} = P_{r1}P_{cb} = 0.69 \times 4880 = 3367$ kPa

$\bar{h}^*_{b1} - \bar{h}_{b1} = 3.81\ \bar{R}T_{cb} = 9674.5$ kJ/kmol, $\bar{s}^*_{b1} - \bar{s}_{b1} = 3.74\ \bar{R} = 31.1$

$\bar{h}^*_{b3} - \bar{h}^*_{b1} = M_bC_{pb}(T_3 - T_{b1}) = 5629.6$ kJ/kmol

Exit: Mix, $T_3 = 120^oC$, $P_3 = 800$ kPa consider this an ideal gas mixture.

Energy Eq.: $\dot{n}_1\bar{h}_{b1} + \dot{n}_2\bar{h}_{a2} + \dot{Q} = \dot{n}_3\bar{h}_3 = \dot{n}_1\bar{h}_{b3} + \dot{n}_2\bar{h}_{a3}$

$\dot{Q} = \dot{n}_1(\bar{h}_{b3} - \bar{h}_{b1}) + \dot{n}_2(\bar{h}_{a3} - \bar{h}_{a2}) = 0.25\ (5629.6 + 9674.5) + 0.75(1973.4)$

$= \mathbf{5306\ kW}$

Entropy Eq.: $\dot{S}_{gen} = \dot{n}_1(\bar{s}_{b3} - \bar{s}_{b1}) + \dot{n}_2(\bar{s}_{a3} - \bar{s}_{a2}) - \dot{Q}/T_H$; $T_H = 150^oC$

$y_a = \dot{n}_2/\dot{n}_{tot} = 0.75$; $y_b = \dot{n}_1/\dot{n}_{tot} = 0.25$

$$\bar{s}_{a3} - \bar{s}_{a2} = M_aC_{pa}\ln\frac{T_3}{T_{a2}} - \bar{R}\ln\frac{y_aP_3}{P_{a2}} = 8.14 \text{ kJ/kmol-K}$$

$$\bar{s}_{b3} - \bar{s}_{b1} = M_bC_{pb}\ln\frac{T_3}{T_{b1}} - \bar{R}\ln\frac{y_bP_3}{P_{b1}} + \bar{s}^*_{b1} - \bar{s}_{b1} =$$

$$= 40.172 + 31.1 = 71.27 \text{ kJ/kmol K}$$

$\dot{S}_{gen} = 0.25 \times 71.27 + 0.75 \times 8.14 - 5306 / 423 = \mathbf{11.38\ kW/K}$

13.99

A modern jet engine operates so that the fuel is sprayed into air at a P, T higher than the fuel critical point. Assume we have a rich mixture of 50% n-octane and 50% air by mole at 500 K and 3.5 MPa near the nozzle exit. Do I need to treat this as a real gas mixture or is an ideal gas assumption reasonable? To answer find Z and the enthalpy departure for the mixture assuming Kay's rule and the generalized charts.

The mole fractions are:

$$y_{C8H18} = 0.5, \quad y_{N2} = 0.5 \times 0.79 = 0.395, \quad y_{O2} = 0.5 \times 0.21 = 0.105$$

Eq.12.5:

$$M_{mix} = \sum y_i M_i = 0.5 \times 114.232 + 0.395 \times 28.013 + 0.105 \times 31.999$$
$$= 71.541$$

Kay's rule Eq.13.86

$$P_{c\ mix} = 0.5 \times 2.49 + 0.395 \times 3.39 + 0.105 \times 5.04 = 3.113 \text{ MPa}$$
$$T_{c\ mix} = 0.5 \times 568.8 + 0.395 \times 126.2 + 0.105 \times 154.6 = 350.5 \text{ K}$$

Reduced properties: $P_r = \frac{3.5}{3.113} = 1.124, \quad T_r = \frac{500}{350.5} = 1.427$

Fig. D.1: **Z = 0.87** I must treat it as a real gas mixture.

Fig. D.2 $h^* - h = 0.70 \times RT_c = 0.70 \times \frac{8.3145}{71.541} \times 350.5 =$ **28.51 kJ/kg**

13.100

A mixture of 60% ethylene and 40% acetylene by moles is at 6 MPa, 300 K. The mixture flows through a preheater where it is heated to 400 K at constant P. Using the Redlich Kwong equation of state with a, b for a mixture find the inlet specific volume. Repeat using Kays rule and the generalized charts.

To do the EOS we need the gas constant, so from Eq.12.5 we get

$$M_{mix} = \sum y_i M_i = 0.6 \times 28.054 + 0.4 \times 26.068 = 27.26$$

$$R_{mix} = 8.3145/27.26 = 0.305 \text{ kJ/kg K}$$

Redlich Kwong EOS the individual component parameters, Eq.13.58, 13.59.

$$a_{C2H4} = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} = 0.42748 \frac{0.2964^2 \times 282.4^{2.5}}{5040} = 9.9863$$

$$a_{C2H2} = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} = 0.42748 \frac{0.3193^2 \times 308.3^{2.5}}{6140} = 11.8462$$

$$b_{C2H4} = 0.08664 \frac{RT_c}{P_c} = 0.08664 \frac{0.2964 \times 282.4}{5040} = 0.001\,439$$

$$b_{C2H2} = 0.08664 \frac{RT_c}{P_c} = 0.08664 \frac{0.3193 \times 308.3}{6140} = 0.001\,389$$

Now the mixture parameters are from eq.13.87 so we need the mass fractions

$$c_{C2H4} = \frac{y\,M}{M_{mix}} = \frac{0.6 \times 28.054}{27.26} = 0.6175, \qquad c_{C2H4} = 1 - c_{C2H4} = 0.3825$$

$$a_{mix} = \left(\sum c_i\, a_i^{1/2}\right)^2 = (0.6175 \times \sqrt{9.9863} + 0.3825 \times \sqrt{11.8462})^2 = 10.679$$

$$b_{mix} = \sum c_i\, b_i = 0.6175 \times 0.001\,439 + 0.3825 \times 0.001\,389 = 0.001\,42$$

Using now eq.13.57: $P = \frac{RT}{v - b} - \frac{a}{v(v + b)T^{1/2}}$

$$6000 = \frac{0.305 \times 300}{v - 0.001\,42} - \frac{10.679}{v(v + 0.001\,42)\,300^{1/2}}$$

By trial and error we find the specific volume, v = **0.006683 m^3/kg**

Kay's rule Eq.13.86

$$P_{c\,mix} = 0.6 \times 5.04 + 0.4 \times 6.14 = 5.48 \text{ MPa}$$

$$T_{c\,mix} = 0.6 \times 282.4 + 0.4 \times 308.3 = 292.8 \text{ K}$$

Reduced properties: $P_r = \frac{6}{5.48} = 1.095, \quad T_r = \frac{300}{292.8} = 1.025$

Fig. D.1: Z = 0.4 (difficult to read)

v = ZRT/P = 0.4 × 0.305 × 300 / 6000 = **0.0061 m^3/kg**

13.101

For the previous problem, find the specific heat transfer using Kay's rule and the generalized charts.

To do the EOS we need the gas constant, so from Eq.12.5 we get

$$M_{mix} = \sum y_i M_i = 0.6 \times 28.054 + 0.4 \times 26.068 = 27.26$$

$$R_{mix} = 8.3145/27.26 = 0.305 \text{ kJ/kg K}$$

$$c_{C2H4} = \frac{y\,M}{M_{mix}} = \frac{0.6 \times 28.054}{27.26} = 0.6175, \qquad c_{C2H4} = 1 - c_{C2H4} = 0.3825$$

$$C_{P\,mix} = \sum c_i C_{P\,i} = 0.6175 \times 1.548 + 0.3825 \times 1.699 = 1.606 \text{ kJ/kg K}$$

Kay's rule Eq.13.86

$$P_{c\,mix} = 0.6 \times 5.04 + 0.4 \times 6.14 = 5.48 \text{ MPa}$$

$$T_{c\,mix} = 0.6 \times 282.4 + 0.4 \times 308.3 = 292.8 \text{ K}$$

Reduced properties 1: $P_{r1} = \frac{6}{5.48} = 1.095, \quad T_{r1} = \frac{300}{292.8} = 1.025$

Fig. D.1: $\left(h_1^* - h_1\right) = 2.1 \times RT_c = 2.1 \times 0.305 \times 292.8 = 187.5$ kJ/kg

Reduced properties 2: $P_{r2} = \frac{6}{5.48} = 1.095, \quad T_{r2} = \frac{400}{292.8} = 1.366$

Fig. D.1: $\left(h_2^* - h_2\right) = 0.7 \times RT_c = 0.7 \times 0.305 \times 292.8 = 62.5$ kJ/kg

The energy equation gives

$$_1q_2 = (h_2 - h_1) = \left(h_2 - h_2^*\right) + \left(h_2^* - h_1^*\right) + \left(h_1^* - h_1\right)$$

$$= -62.5 + 1.606\,(400 - 300) + 187.5$$

= **285.6 kJ/kg mix**

13.102

One kmol/s of saturated liquid methane, CH_4, at 1 MPa and 2 kmol/s of ethane, C_2H_6, at 250°C, 1 MPa are fed to a mixing chamber with the resultant mixture exiting at 50°C, 1 MPa. Assume that Kay's rule applies to the mixture and determine the heat transfer in the process.

Control volume the mixing chamber, inlet CH_4 is 1, inlet C_2H_6 is 2 and the exit state is 3. Energy equation is

$$\dot{Q}_{CV} = \dot{n}_3 \bar{h}_3 - \dot{n}_1 \bar{h}_1 - \dot{n}_2 \bar{h}_2$$

Select the ideal gas reference temperature to be T_3 and use the generalized charts for all three states.

$P_{r1} = P_{rsat} = 1/4.60 = 0.2174 \;\Rightarrow\; T_{rsat} = 0.783,$

$T_1 = 0.783 \times 190.4 = 149.1 \text{ K}, \quad \Delta h_1 = 4.57$

$P_{r2} = 1/4.88 = 0.205, \quad T_{r2} = 523/305.4 = 1.713, \quad \Delta h_2 = 0.08$

$\bar{h}_1 = \bar{C}_1(T_1 - T_3) - \Delta h_1 \bar{R}T_c = 36.15(149.1 - 323.2) - 4.57 \times 8.3145 \times 190.4$
$= -13528 \text{ kJ/kmol}$

$\bar{h}_2 = \bar{C}_2(T_2 - T_3) - \Delta h_2 \bar{R}T_c = 53.11(250 - 50) - 0.08 \times 8.3145 \times 305.4$
$= 10\,419 \text{ kJ/kmol}$

Kay's rule Eq.13.86

$T_{cmix} = (1 \times 190.4 + 2 \times 305.4)/3 = 267.1 \text{ K}$

$P_{cmix} = (1 \times 4.60 + 2 \times 4.88)/3 = 4.79 \text{ MPa}$

$T_{r3} = 323.2/267.1 = 1.21, \quad P_{r3} = 1/4.79 = 0.21, \quad \Delta h_3 = 0.15$

$\bar{h}_3 = 0 - 0.15 \times 267.1 \times 8.3145 = -333 \text{ kJ/kmol}$

$\dot{Q}_{CV} = 3(-333) - 1(-13528) - 2(10\,419) = \mathbf{-8309 \text{ kW}}$

13.103

A piston/cylinder initially contains propane at T = -7°C, quality 50%, and volume 10L. A valve connecting the cylinder to a line flowing nitrogen gas at T = 20°C, P = 1 MPa is opened and nitrogen flows in. When the valve is closed, the cylinder contains a gas mixture of 50% nitrogen, 50% propane on a mole basis at T = 20°C, P = 500 kPa. What is the cylinder volume at the final state, and how much heat transfer took place?

State 1: Propane, $T_1 = -7^oC$, $x_1 = 0.5$, $V_1 = 10$ L

$T_c = 369.8$ K, $P_c = 4.25$ kPa, $C_P = 1.679$ kJ/kg-K, M = 44.097 kg/kmol

Fig. D.1: $T_{r1} = 0.72$, $P_{r1} = 0.12$, $P_1 = P_{r1}P_c = 510$ kPa

Fig. D.1: $Z_{f1} = 0.020$, $Z_{g1} = 0.88$, $Z_1 = (1 - x_1)Z_{f1} + x_1Z_{g1} = 0.45$

$n_1 = P_1V_1/(Z_1\bar{R}T_1) = 510 \times 0.01/(0.45 \times 8.3145 \times 266.2) = 0.00512$ kmol

$\bar{h}_1 = \bar{h}^*_{1o} + \bar{C}_P(T_1 - T_o) + (\bar{h}_1 - \bar{h}^*_1)$; $\bar{h}^*_{1o} = 0$,

$(\bar{h}^*_1 - \bar{h}_1)_f / \bar{R}T_c = 4.79$, $(\bar{h}^*_1 - \bar{h}_1)_g / \bar{R}T_c = 0.25$

$\bar{h}^*_1 - \bar{h}_1 = (1 - x_1)(\bar{h}^*_1 - \bar{h}_1)_f + x_1 (\bar{h}^*_1 - \bar{h}_1)_g = 7748$ kJ/kmol

$\bar{h}_1 = 0 + 1.679 \times 44.094(-7 - 20) - 7748 = -9747$ kJ/kmol

Inlet: Nitrogen, $T_i = 20^oC$, $P_i = 1.0$ MPa,

$T_c = 126.2$ K, $P_c = 3.39$ MPa, $C_{pn} = 1.042$ kJ/kg-K, M = 28.013 kg/kmol

$T_{ri} = 2.323$, $P_{ri} = 0.295$, $\bar{h}^*_i - \bar{h}_i = 0.06 \times 8.3145 \times 126.2 = 62.96$ kJ/kmol

$\bar{h}_i = \bar{h}^*_{io} + \bar{C}_{Pn}(T_i - T_o) + (\bar{h}_i - \bar{h}^*_i)$; $\bar{h}^*_{io} = 0$, $T_i - T_o = 0$

State 2: 50% Propane, 50% Nitrogen by mol, $T_2 = 20^oC$, $P_2 = 500$ kPa

$T_{cmix} = \Sigma y_iT_{ci} = 248$ K, $P_{cmix} = \Sigma y_iP_{ci} = 3.82$ MPa

$T_{r2} = 1.182$, $P_{r2} = 0.131$, $Z_2 = 0.97$, $(\bar{h}^*_2 - \bar{h}_2)/\bar{R}T_c = 0.06$

$\bar{h}_2 = \bar{h}^*_{2o} + \bar{C}_{Pmix}(T_2 - T_o) + (\bar{h}_2 - \bar{h}^*_2)$; $\bar{h}^*_{2o} = 0$, $T_2 - T_o = 0$

a) $n_i = n_1$ => $n_2 = n_1 + n_i = 0.1024$, $V_2 = n_2Z_2\bar{R}T_2/P_2 =$ **0.0484 m^3**

b) 1st Law: $Q_{cv} + n_i\bar{h}_i = n_2\bar{u}_2 - n_{21}\bar{u}_{21} + W_{cv}$; $\bar{u} = \bar{h} - P\bar{v}$

$W_{cv} = (P_1 + P_2)(V_2 - V_1)/2 = 19.88$ kJ

$Q_{cv} = n_2\bar{h}_2 - n_1\bar{h}_1 - n_i\bar{h}_i - P_2V_2 + P_1V_1 + W_{cv}$

$\bar{h}_i = -62.96$ kJ/kmol, $\bar{h}_2 = -123.7$ kJ/kmol, $Q_{cv} =$ **50.03 kJ**

13.104

Consider the following reference state conditions: the entropy of real saturated liquid methane at −100°C is to be taken as 100 kJ/kmol K, and the entropy of hypothetical ideal gas ethane at −100°C is to be taken as 200 kJ/kmol K. Calculate the entropy per kmol of a real gas mixture of 50% methane, 50% ethane (mole basis) at 20°C, 4 MPa, in terms of the specified reference state values, and assuming Kay's rule for the real mixture behavior.

CH_4: $T_0 = -100\ ^oC$, $\bar{s}_{LIQ\,0} = 100$ kJ/kmol K

C_2H_6: $T_0 = -100\ ^oC$, $P_0 = 1$ MPa, $\bar{s}^*_0 = 200$ kJ/kmol K

Also for CH_4: $T_C = 190.4$ K, $P_C = 4.60$ MPa

For a 50% mixture Kay's rule Eq.13.86:

$$T_{cmix} = 0.5 \times 190.4 + 0.5 \times 305.4 = 247.9\ K$$

$$P_{cmix} = 0.5 \times 4.60 + 0.5 \times 4.88 = 4.74\ MPa$$

IG MIX at T_0(=-100 °C), P_0(=1 MPa):

CH_4: $T_{r0} = 0.91$, $P_G = 0.57 \times 4.60 = 2.622$ MPa

$$\bar{s}^*_{0\ CH4} = \bar{s}_{LIQ\ 0\ P_G} + (\bar{s}^*-\bar{s}_{LIQ})_{at\ P_G} - \bar{R}\ln(P_0/P_G)$$

$$= 100 + 4.01\times8.3145 - 8.3145\ln(1/2.622) = 141.36$$

$$\bar{s}^*_{0\ MIX} = 0.5\times141.36 + 0.5\times200 - 8.3145(0.5\ln 0.5 + 0.5\ln 0.5) = 176.44$$

$$\bar{C}_{P0\ MIX} = 0.5\times16.04\times2.254 + 0.5\times30.07\times1.766 = 44.629$$

$$\bar{s}^*_{TP\ MIX} = 176.44 + 44.629\ln\frac{293.2}{173.2} - 8.3145\ln\frac{4}{1} = 188.41\ \text{kJ/kmol K}$$

For the mixture at T, P: $T_r = 1.183$, $P_r = 0.844$

Entropy departure $\bar{s}^*_{TP\ MIX} - \bar{s}_{TP\ MIX} = 0.4363\times8.3145 = 3.63$ kJ/kmol K

Therefore,

$$\bar{s}_{TP\ MIX} = 188.41 - 3.63 = \mathbf{184.78\ kJ/kmol\ K}$$

An alternative is to form the ideal gas mixture at T, P instead of at T_0, P_0 :

$$\bar{s}^*_{TP\ CH4} = \underset{P_G,\ T_0}{\bar{s}_{LIQ\ 0}} + \underset{\text{at } P_G,\ T_0}{(\bar{s}^*-\bar{s}_{LIQ})} + \bar{C}_{P0\ CH4}\ln\frac{T}{T_0} - \bar{R}\ln\frac{P}{P_G}$$

$$= 100 + 33.34 + 16.04\times2.254 \ln\frac{293.2}{173.2} - 8.3145 \ln\frac{4}{2.6}$$

$$= 100 + 33.34 + 19.03 - 3.53 = 148.84 \text{ kJ/kmol K}$$

$$\bar{s}^*_{TP\ C2H6} = 200 + 30.07\times1.766 \ln\frac{293.2}{173.2} - 8.3145 \ln\frac{4}{1}$$

$$= 200 + 27.96 - 11.53 = 216.43 \text{ kJ/kmol K}$$

$$\bar{s}^*_{TP\ MIX} = 0.5\times148.84 + 0.5\times216.43$$

$$- 8.3145(0.5 \ln 0.5 + 0.5 \ln 0.5) = 188.41 \text{ kJ/kmol K}$$

$$\bar{s}_{TP\ MIX} = 188.41 - 3.63 = \mathbf{184.78\ kJ/kmol\ K}$$

13.105

A cylinder/piston contains a gas mixture, 50% CO2 and 50% C2H6 (mole basis) at 700 kPa, 35°C, at which point the cylinder volume is 5 L. The mixture is now compressed to 5.5 MPa in a reversible isothermal process. Calculate the heat transfer and work for the process, using the following model for the gas mixture:

a. Ideal gas mixture.

b. Kay's rule and the generalized charts.

a) Ideal gas mixture

$U_2 - U_1 = mC_{v\,mix}(T_2 - T_1) = 0$

$Q_{12} = W_{12} = \int P\,dV = P_1V_1 \ln(V_2/V_1) = - P_1V_1 \ln(P_2/P_1)$

$= - 700 \times 0.005 \ln(5500/700) =$ **-7.71 kJ**

b) Kay's rule

$T_{cmix} = 0.5 \times 304.1 + 0.5 \times 305.4 = 304.75\ \text{K}$

$P_{cmix} = 0.5 \times 7.38 + 0.5 \times 4.88 = 6.13\ \text{MPa}$

$T_{r1} = 308.15/304.75 = 1.011, \quad P_{r1} = 0.7/6.13 = 0.1142$

$Z_1 = 0.96, \quad \Delta h_1 = 0.12, \quad \Delta s_1 = 0.08$

$$n = P_1V_1/Z_1\bar{R}\,T_1 = \frac{700*0.005}{0.962*8.3145*308.15} = 0.00142\ \text{kmol}$$

$T_{r2} = T_{r1}\ , \quad P_{r2} = 5.5/6.13 = 0.897,$

$Z_2 = 0.58, \quad \Delta h_2 = 1.35, \quad \Delta s_2 = 1.0$

$\bar{h}_2 - \bar{h}_1 = (\bar{h}_2 - \bar{h}_1) - \bar{R}\,T_c(\Delta h_2 - \Delta h_1)$

$= 0 - 8.3145 \times 304.75(1.35 - 0.12) = - 3117$

$\bar{u}_2 - \bar{u}_1 = \bar{h}_2 - \bar{h}_1 + \bar{R}T(Z_1 - Z_2) = - 3117$

$+ 8.3145 \times 308.15(0.96 - 0.58) = -2143\ \text{kJ/kmol}$

$Q_{12} = nT(\bar{s}_2 - \bar{s}_1)_T = 0.00142 \times 308.15 \times 8.3145[\ 0 - \ln(5.5/0.7) -1.0$

$+ 0.08\ ] =$ **$- 10.85$ kJ**

$W_{12} = Q_{12} - n(\bar{u}_2 - \bar{u}_1) = -10.85 - 0.00142(-2143) =$ **$- 7.81$ kJ**

13.106

A cylinder/piston contains a gas mixture, 50% CO2 and 50% C2H6 (mole basis) at 700 kPa, 35°C, at which point the cylinder volume is 5 L. The mixture is now compressed to 5.5 MPa in a reversible isothermal process. Calculate the heat transfer and work for the process, using the following model for the gas mixture:

a. Ideal gas mixture.

b. The van der Waals equation of state.

a) Ideal gas mixture

$U_2 - U_1 = mC_{v\,mix}(T_2 - T_1) = 0$

$Q_{12} = W_{12} = \int P\,dV = P_1V_1 \ln(V_2/V_1) = - P_1V_1 \ln(P_2/P_1)$

$= - 700 \times 0.005 \ln(5500/700) =$ **-7.71 kJ**

b) van der waal's equation

For CO_2 :

$b = \bar{R}\,T_c/8P_c = 8.3145 \times 304.1/8 \times 7380 = 0.04282$

$a = 27\,P_c\,b^2 = 27 \times 7380 \times 0.04282^2 = 365.45$

For C_2H_6 :

$b = \bar{R}\,T_c/8P_c = 8.3145 \times 305.4/8 \times 4880 = 0.06504$

$a = 27\,P_c\,b^2 = 27 \times 4880 \times 0.06504^2 = 557.41$

$a_{mix} = (0.5\sqrt{365.45} + 0.5\sqrt{557.41})^2 = 456.384$

$b_{mix} = 0.5 \times 0.04282 + 0.5 \times 0.06504 = 0.05393$

$$\frac{8.3145*308.2}{\bar{v}_1 - 0.05393} - \frac{456.384}{\bar{v}_1^2} - 700 = 0$$

By trial and error: $\bar{v}_1 = 3.5329$ m^3/kmol

$$\frac{8.3145*308.2}{\bar{v}_2 - 0.05393} - \frac{456.384}{\bar{v}_2^2} - 5500 = 0$$

By trial and error: $\bar{v}_2 = 0.2815$ m^3/kmol

$n = V_1/\bar{v}_1 = 0.005/3.5329 = 0.00142$

$$Q_{12} = nT(\bar{s}_2 - \bar{s}_1)_T = n\,\bar{R}\,T \ln\frac{\bar{v}_2 - b}{\bar{v}_1 - b}$$

$$= 0.00142 \times 8.3145 \times 308.2 \ln\frac{0.2815 - 0.05392}{3.5329 - 0.05392} = \mathbf{-\ 9.93\ kJ}$$

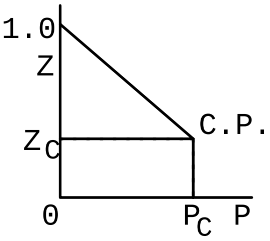
$U_2\text{-}U_1 = 0.00142 \times 456.39(3.5329^{-1} - 0.2815^{-1}) = -2.12$ kJ

$Q_{12} = U_2\text{-}U_1 + W_{12} \Rightarrow W_{12} = -9.93 -(-2.12) =$ **-7.81 kJ**

Review Problems

13.107

Consider a straight line connecting the point $P = 0$, $Z = 1$ to the critical point $P = P_C$, $Z = Z_C$ on a Z versus P compressibility diagram. This straight line will be tangent to one particular isotherm at low pressure. The experimentally determined value is about 0.8 T_C. Determine what value of reduced temperature is predicted by an equation of state, using the van der Waals equation and the Redlich–Kwong equation. See also note for Problem 13.56.



$$\text{slope} = \frac{Z_C - 1}{P_C - 0}$$

But also equals $\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T$ for $T = T'$

From solution **13.25**

$$\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = \lim_{P\to 0}\frac{Z-1}{P-0} = \frac{1}{RT}\lim_{P\to 0}\left(v - \frac{RT}{P}\right)$$

VDW: using solution **13.25:** $\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{Z_C - 1}{P_C} = \frac{1}{RT'}\left[b - \frac{a}{RT'}\right]$

or $$\left(\frac{1-Z_C}{P_C}\right)(RT')^2 + bRT' - a = 0$$

Substituting $Z_C = \frac{3}{8}$, $a = \frac{27}{64}\frac{R^2T_C^2}{P_C}$, $b = \frac{RT_C}{8P_C}$

$40\,T_r'^2 + 8\,T_r' - 27 = 0$ solving, $T_r' = \mathbf{0.727}$

Redlich-Kwong: using solution **13.25**,

$$\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{Z_C - 1}{P_C} = \frac{1}{RT'}\left[b - \frac{a}{RT'^{\,3/2}}\right] \quad \text{or} \quad \left(\frac{1-Z_C}{P_C}\right)R^2T'^{\,5/2} + bRT'^{\,3/2} - a = 0$$

Substitute $Z_C = \frac{1}{3}$, $a = 0.42748\frac{R^2T_C^{5/2}}{P_C}$, $b = 0.08664\frac{RT_C}{P_C}$

get $$\frac{2}{3}T_r'^{\,5/2} + 0.086\,64\,T_r'^{\,3/2} - 0.427\,48 = 0$$

solving, $T_r' = \mathbf{0.787}$

13.108

A 200-L rigid tank contains propane at 400 K, 3.5 MPa. A valve is opened, and propane flows out until half the initial mass has escaped, at which point the valve is closed. During this process the mass remaining inside the tank expands according to the relation $Pv^{1.4}$ = constant. Calculate the heat transfer to the tank during the process.

C_3H_8: $V = 200$ L, $T_1 = 400$ K, $P_1 = 3.5$ MPa

Flow out to $m_2 = m_1/2$; $Pv^{1.4}$ = const inside

$$T_{r1} = \frac{400}{369.8} = 1.082,\ P_{r1} = \frac{3.5}{4.25} = 0.824 \quad \text{Fig D.1: } Z_1 = 0.74$$

$$v_1 = \frac{0.74 \times 0.188\ 55 \times 400}{3500} = 0.01594,\ \ v_2 = 2v_1 = 0.03188$$

$$m_1 = \frac{0.2}{0.015\ 94} = 12.55 \text{ kg}, \quad m_2 = \frac{1}{2} m_1 = 6.275 \text{ kg},$$

$$P_2 = P_1 \left(\frac{v_1}{v_2}\right)^{1.4} = \frac{3500}{2^{1.4}} = 1326 \text{ kPa}$$

$$\left.\begin{aligned} P_{r2} &= \frac{1.326}{4.25} = 0.312 \\ P_2 v_2 &= Z_2 R T_2 \end{aligned}\right\} \begin{aligned} &\text{Trial \& error: saturated with} \\ &T_2 = 0.826 \times 369.8 = 305.5 \text{ K \&} \\ &Z_2 = \frac{1326 \times 0.03188}{0.188\ 55 \times 305.5} = 0.734 \end{aligned}$$

$$Z_2 = Z_{F2} + x_2(Z_{G2} - Z_{F2}) = 0.734 = 0.05 + x_2(0.78\text{-}0.05) \quad \Rightarrow \quad x_2 = 0.937$$

$$(h_1^*\text{-}h_1) = 0.188\ 55 \times 369.8(0.9) = 62.8$$

$$(h_2^*\text{-}h_1^*) = 1.6794(305.5\text{-}400) = -158.7$$

$$(h_2^*\text{-}h_2) = (h_2^*\text{-}h_{F2}) - x_2 h_{FG2} = 0.188\ 55 \times 369.8 \Big[4.41 - 0.937(4.41\text{-}0.55)\Big] = 55.3$$

1st law: $Q_{CV} = m_2 h_2 - m_1 h_1 + (P_1\text{-}P_2)V + m_e h_{e\ AVE}$

Let $h_1^* = 0$ then $\quad h_1 = 0 + (h_1\text{-}h_1^*) = -62.8$

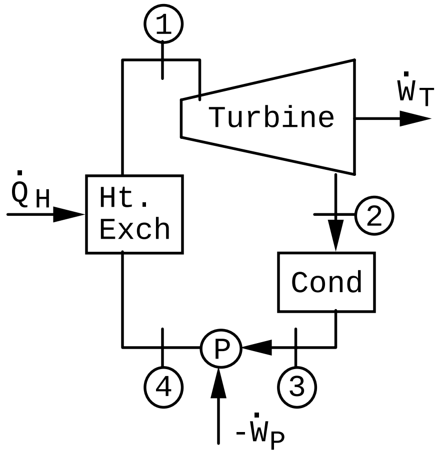
$$h_2 = h_1^* + (h_2^*\text{-}h_1^*) + (h_2\text{-}h_2^*) = 0 - 158.7 - 55.3 = -214.0$$

$$h_{e\ AVE} = (h_1+h_2)/2 = -138.4$$

$$Q_{CV} = 6.275(-214.0) - 12.55(-62.8) + (3500\text{-}1326) \times 0.2 + 6.275(-138.4) = \mathbf{-981.4\ kJ}$$

13.109

A newly developed compound is being considered for use as the working fluid in a small Rankine-cycle power plant driven by a supply of waste heat. Assume the cycle is ideal, with saturated vapor at 200°C entering the turbine and saturated liquid at 20°C exiting the condenser. The only properties known for this compound are molecular weight of 80 kg/kmol, ideal gas heat capacity C_{PO}= 0.80 kJ/kg K and T_C = 500 K, P_C = 5 MPa. Calculate the work input, per kilogram, to the pump and the cycle thermal efficiency.



$T_1 = 200^oC = 473.2$ K, $x_1 = 1.0$

$T_3 = 20^oC = 293.2$ K, $x_3 = 0.0$

Properties known:

$M = 80$, $C_{PO} = 0.8$ kJ/kg K

$T_C = 500$ K, $P_C = 5.0$ MPa

$$T_{r1} = \frac{473.2}{500} = 0.946\ ,\quad T_{r3} = \frac{293.2}{500} = 0.586$$

$R = \bar{R}/M = 8.31451/80 = 0.10393$ kJ/kg K

From Fig. D.1,

$P_{r1} = 0.72$, $P_1 = 0.72 \times 5 = 3.6 \text{ MPa} = P_4$

$P_{r3} = 0.023$, $P_3 = 0.115 \text{ MPa} = P_2$, $Z_{F3} = 0.004$

$$v_{F3} = \frac{Z_{F3}RT_3}{P_3} = \frac{0.004 \times 0.10393 \times 293.2}{115} = 0.00106 \text{ m}^3\text{/kg}$$

$$w_P = -\int_3^4 v dP \approx v_{F3}(P_4 - P_3) = -0.00106(3600-115) = \mathbf{-3.7\ kJ/kg}$$

$q_H + h_4 = h_1$, but $h_3 = h_4 + w_P$ => $q_H = (h_1 - h_3) + w_P$

From Fig. D.2:

$(h^*_1 - h_1) = RT_C \times 1.25 = 0.103\,93 \times 500 \times 1.25 = 64.9$ kJ/kg

$(h^*_3 - h_3) = 0.103\,93 \times 500 \times 5.2 = 270.2$ kJ/kg

$(h^*_1 - h^*_3) = C_{P0}(T_1 - T_3) = 0.80(200-20) = 144.0$ kJ/kg

$(h_1 - h_3) = -64.9 + 144.0 + 270.2 = 349.3$ kJ/kg

$q_H = 349.3 + (-3.7) = 345.6$ kJ/kg

Turbine, $(s_2 - s_1) = 0 = -(s_2^* - s_2) + (s_2^* - s_1^*) + (s_1^* - s_1)$

From Fig. D.3,

$(s_1^* - s_1) = 0.10393 \times 0.99 = 0.1029$ kJ/kg K

$$(s_2^* - s_1^*) = 0.80 \ln \frac{293.2}{473.2} - 0.103\,93 \ln \frac{115}{3600} = -0.0250$$

Substituting,

$s_2^* - s_2 = +0.1029 - 0.0250 = 0.0779 = (s_2^* - s_{F2}) - x_2 s_{FG2}$

$0.0779 = 0.103\,93 \times 8.85 - x_2 \times 0.103\,93(8.85 - 0.06) \quad \Rightarrow \quad x_2 = 0.922$

$(h_2^* - h_2) = (h_2^* - h_{F2}) - x_2 h_{FG2}$

From Fig. D.2,

$h_{FG2} = 0.10393 \times 500\,(5.2 - 0.07) = 266.6$

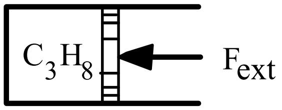
$(h_2^* - h_2) = 270.2 - 0.922 \times 266.6 = 25.0$

$w_T = (h_1 - h_2) = -64.9 + 144.0 + 25.0 = 104.1$ kJ/kg

$$\eta_{TH} = \frac{w_{NET}}{q_H} = \frac{104.1 - 3.7}{345.6} = \mathbf{0.29}$$

13.110

A cylinder fitted with a movable piston contains propane, initially at 67°C and 50 % quality, at which point the volume is 2 L. The piston has a cross-sectional area of 0.2 m^2. The external force on the piston is now gradually reduced to a final value of 85 kN, during which process the propane expands to ambient temperature, 4°C. Any heat transfer to the propane during this process comes from a constant-temperature reservoir at 67°C, while any heat transfer from the propane goes to the ambient. It is claimed that the propane does 30 kJ of work during the process. Does this violate the second law?



+Q from T_{res} = 67°C
-Q to Environment T_o = 4°C
$F_{ext\,2}$ = 85 kN

Propane: T_c= 369.8 K, P_c = 4.25 MPa, R = 0.18855 kJ/kg K, C_p = 1.679 kJ/kg K

State 1: $T_1 = 67^oC = 340.2$ K, $x_1 = 0.5$, $V_1 = 2.0$ L

$T_{r1} = 0.92$, Fig D.1, $P_{r1} = 0.61$, $P_1 = P_{r1}P_c = 2.592$ MPa

$Z_{f1} = 0.10$, $Z_{g1} = 0.64$, $Z_1 = (1 - x_1)Z_{f1} + x_1Z_{g1} = 0.37$

$$m = \frac{P_1V_1}{Z_1RT_1} = 0.218 \text{ kg},\ (h^*_1 - h_1)_f = 3.95\ RT_c\ ,\ (h^*_1 - h_1)_g = 1.03\ RT_c$$

$$(s^*_1 - s_1)_f = 4.0\ R\ ,\quad (s^*_1 - s_1)_g = 0.82\ R$$

State 2: $T_2 = 4^oC = 277.2$ K, $F_{ext\,2} = 85$ kN

$T_{r2} = 0.75$, $P^{sat}_2 = P^{sat}_{r2}P_c = 0.165 \times 4250 = 701$ kPa

$P_2 = F_{ext\,2}/A_p = 425$ kPa, $P_2 < P^{sat}_2$ → State 2 is a vapor

$P_{r2} = 0.10$, $Z_2 = 0.92$, $V_2 = mZ_2RT_2/P_2 = 0.0247\ m^3$

$h^*_2 - h_2 = 0.18\ RT_c = 12.6$ kJ/kg, $s^*_2 - s_2 = 0.16\ R = 0.0302$ kJ/kg K

1st Law: ${}_1Q_2 = m(u_2 - u_1) + {}_1W_2$; ${}_1W_2 = 30$ kJ, u = h - Pv

$${}_1Q_2 = m(h_2 - h_1) - P_2V_2 + P_1V_1 + {}_1W_2$$

$$(h_2 - h_1) = (h_2 - h^*_2) + (h^*_2 - h^*_1) + (h^*_1 - h_1)$$

$$(h^*_1 - h_1) = (1 - x_1)(h^*_1 - h_1)_f + x_1\,(h^*_1 - h_1)_g = \ 173.6 \text{ kJ/kg}$$

$h^*_2 - h^*_1 = C_p(T_2 - T_1) = -105.8$ kJ/kg

${}_1Q_2 = 0.218\ (-12.6 - 105.8 + 173.6) - 425\times0.0247 + 2592\times0.002 + 30$

$= 36.7$ kJ

2nd Law: $\Delta S_{net} = m(s_2 - s_1) - \frac{{}_1Q_2}{T}$; $T_{res} = 67^oC = 340.2$ K

$s_2 - s_1 = \left(s_2 - s^*_2\right) + \left(s^*_2 - s^*_1\right) + \left(s^*_1 - s_1\right)$

$s^*_1 - s_1 = (1 - x_1)\left(s^*_1 - s_1\right)_f + x_1\left(s^*_1 - s_1\right)_g = 0.4544$ kJ/kg-K

$s^*_2 - s^*_1 = C_p\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} = -0.0030$ kJ/kg K

$\Delta S_{net} = 0.218\ (-0.0302-0.0030+0.4544) - 36.7/340.2 =$ **-0.0161 kJ/K;**

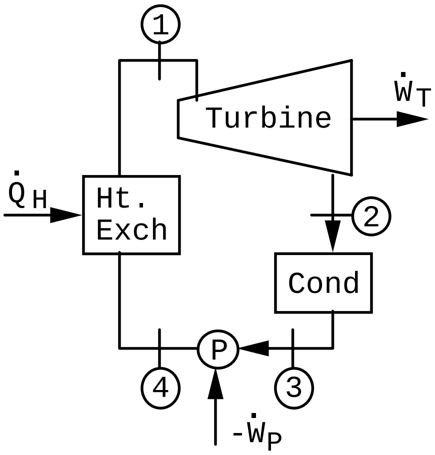
$\Delta S_{net} < 0$ Process is Impossible

13.111

One kilogram per second water enters a solar collector at 40°C and exits at 190°C, as shown in Fig. P13.111. The hot water is sprayed into a direct-contact heat exchanger (no mixing of the two fluids) used to boil the liquid butane. Pure saturated-vapor butane exits at the top at 80°C and is fed to the turbine. If the butane condenser temperature is 30°C and the turbine and pump isentropic efficiencies are each 80%, determine the net power output of the cycle.

H_2O cycle: solar energy input raises 1 kg/s of liquid H_2O from 40°C to 190°C. Therefore, corresponding heat input to the butane in the heat exchanger is

$$\dot{Q}_H = \dot{m}(h_{F\,190\,C} - h_{F\,40\,C})_{H2O} = 1(807.62-167.57) = 640.05 \text{ kW}$$



C_4H_{10} cycle

$T_1 = 80\ ^oC,\ x_1 = 1.0\ ;\ T_3 = 30\ ^oC,\ x_3 = 0.0$

$\eta_{ST} = \eta_{SP} = 0.80$

$$T_{r1} = \frac{353.2}{425.2} = 0.831$$

From D.1, D.2 and D.3:

$P_1 = 0.325 \times 3800 = 1235$ kPa

$(h^*_1 - h_1) = 0.143\ 04 \times 425.2 \times 0.56 = 34.1$

$(s^*_1 - s_1) = 0.143\ 04 \times 0.475 = 0.0680$

$$T_{r3} = \frac{303.2}{425.2} = 0.713$$

From D.1, D.2 and D.3: $P_3 = 0.113 \times 3800 = 429$ kPa

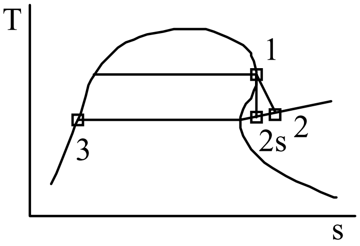
sat. liq.: $(h^* - h_F) = RT_C \times 4.81 = 292.5$; $(s^* - s_F) = R \times 6.64 = 0.950$

sat. vap.: $(h^* - h_G) = RT_C \times 0.235 = 14.3$; $(s^* - s_G) = R \times 0.22 = 0.031$

Because of the combination of properties of C_4H_{10} (particularly the large C_{P0} /R), s_1 is larger than s_G at T_3. To demonstrate,

$$(s^*_1 - s^*_{G3}) = 1.7164 \ln\frac{353.2}{303.2} - 0.143\ 04 \ln\frac{1235}{429} = 0.1107$$

$$(s_1 - s_{G3}) = -0.0680 + 0.1107 + 0.031 = +0.0737 \text{ kJ/kg K}$$



so that T_{2S} will be $> T_3$, as shown in the T-s diagram. A number of other heavy hydrocarbons also exhibit this behavior.

Assume $T_{2S} = 315$ K, $T_{r2S} = 0.741$

From D.2 and D.3:

$$(h^*_{2S}-h_{2S}) = RT_C\times 0.21 = 12.8 \quad \text{and} \quad (s^*_{2S}-s_{2S}) = R\times 0.19 = 0.027$$

$$(s^*_1-s^*_{2S}) = 1.7164 \ln\frac{353.2}{315} - 0.143\,04 \ln\frac{1235}{429} = +0.0453$$

$$(s_1-s_{2S}) = -0.0680 + 0.0453 + 0.027 \approx 0$$

$$\Rightarrow T_{2S} = 315 \text{ K}$$

$$(h^*_1-h^*_{2S}) = 1.7164(353.2-315) = 65.6$$

$$w_{ST} = h_1-h_{2S} = -34.1 + 65.6 + 12.8 = 44.3 \text{ kJ/kg}$$

$$w_T = \eta_S\times w_{ST} = 0.80\times 44.3 = 35.4 \text{ kJ/kg}$$

At state 3,

$$v_3 = \frac{0.019\times 0.143\,04\times 303.2}{429} = 0.001\,92 \text{ m}^3\text{/kg}$$

$$-w_{SP} \approx v_3(P_4-P_3) = 0.001\,92(1235-429) = 1.55 \text{ kJ/kg}$$

$$-w_P = \frac{-w_{SP}}{\eta_{SP}} = \frac{1.55}{0.8} = 1.94 \text{ kJ/kg}$$

$$w_{NET} = w_T + w_P = 35.4 - 1.94 = 33.46 \text{ kJ/kg}$$

For the heat exchanger,

$$\dot{Q}_H = 640.05 = \dot{m}_{C4H10}(h_1-h_4)$$

But $h_1-h_4 = h_1-h_3+w_P$

$$h_1-h_3 = (h_1-h^*_1) + (h^*_1-h^*_3) + (h^*_3-h_3)$$

$$= -34.1 + 1.716(80 - 30) + 292.5 = 344.2 \text{ kJ/kg}$$

Therefore,

$$\dot{m}_{C4H10} = \frac{640.05}{344.2-1.94} = 1.87 \text{ kg/s}$$

$$\dot{W}_{NET} = \dot{m}_{C4H10}w_{NET} = 1.87 \times 33.46 = \mathbf{62.57\ kW}$$

13.112

A piston/cylinder contains ethane gas, initially at 500 kPa, 100 L, and at ambient temperature, 0°C. The piston is now moved, compressing the ethane until it is at 20°C, with a quality of 50%. The work required is 25% more than would have been required for a reversible polytropic process between the same initial and final states. Calculate the heat transfer and the net entropy change for the process.

Ethane: $T_c = 305.4$ K, $P_c = 4.88$ MPa,

$R = 0.2765$ kJ/kg-K, $C_p = 1.766$ kJ/kg K

State 1: $T_{r1} = 0.895$, $P_{r1} = 0.102$ → $Z_1 = 0.95$

$v_1 = Z_1RT_1/P_1 = 0.1435\ \text{m}^3/\text{kg}$, $m_1 = V_1/v_1 = 0.697$ kg

$(h_1^* - h_1) = 0.13RT_c = 11.0$ kJ/kg, $(s_1^* - s_1) = 0.09\ R = 0.025$ kJ/kg K

State 2: $T_2 = 20^oC$, $x_2 = 0.5$, ${}_1W_2 = 1.25W_{rev}$

$T_{r2} = 0.96$, $P_{r2} = 0.78$, $P_2 = P_{r2}P_c = 3806$ kPa

$Z_{f2} = 0.14$, $Z_{g2} = 0.54$, $Z_2 = (1 - x_2)Z_f + x_2Z_g = 0.34$

$(h_2^* - h_2) = (1 - x_2)\ 3.65\ RT_c + x_2\ (1.39\ RT_c) = 212.8$ kJ/kg

$(s_2^* - s_2) = (1 - x_2)\ 3.45\ R + x_2 \times 1.10\ R = 0.629$ kJ/kg K

$v_2 = Z_2RT_2/P_2 = 0.0072\ \text{m}^3/\text{kg}$, $V_2 = mv_2 = 0.005\ \text{m}^3$

$$P_1V_1^n = P_2V_2^n,\quad \ln\frac{P_2}{P_1} = n \ln\frac{V_1}{V_2} \rightarrow n = 0.6783$$

$$W_{rev} = \int P\,dV = \frac{P_2V_2 - P_1V_1}{1 - n} = -96.3\ \text{kJ},\ {}_1W_2 = 1.25W_{rev} = -120.4\ \text{kJ}$$

a) 1^{st} Law: ${}_1Q_2 = m(u_2 - u_1) + {}_1W_2$; $u = h - Pv$

$h_2 - h_1 = (h_2 - h_2^*) + (h_2^* - h_1^*) + (h_1^* - h_1)$

$= -212.8 + 1.766(20 - 0) + 11.0 = -166.5$ kJ/kg

$u_2 - u_1 = (h_2 - h_1) - (P_2v_2 - P_1v_1) = -122.2$ kJ/kg

${}_1Q_2 = 0.697(-122.2) - 120.4 =$ **-205.6 kJ**

b) 2^{nd} Law: $\Delta S_{net} = m(s_2 - s_1) - {}_1Q_2 / T_o$; $T_o = 0^oC$

$s_2 - s_1 = (s_2 - s_2^*) + (s_2^* - s_1^*) + (s_1^* - s_1)$

$(s_2^* - s_1^*) = C_p \ln(T_2 / T_1) - R \ln(P_2 / P_1) = -0.436$ kJ/kg K,

$$\Delta S_{net} = 0.697(-0.629 - 0.436 + 0.025) + \frac{205.6}{273.2} = \mathbf{0.028\ kJ/K}$$

13.113

An experiment is conducted at –100°C inside a rigid sealed tank containing liquid R-22 with a small amount of vapor at the top. When the experiment is done the container and the R-22 warms up to room temperature of 20°C. What is the pressure inside the tank during the experiment? If the pressure at room temperature should not exceed 1 MPa, what is the maximum percent of liquid by volume that can be used during the experiment?

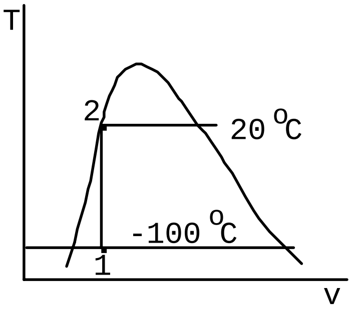
R-22 tables Go to -70 ^{o}C

a) For $h_{FG} \approx$ const &

$v_{FG} \approx v_G \approx RT/P_G$

$$\ln\frac{P_{G1}}{P_{G0}} \approx \frac{h_{FG}}{R}\left[\frac{1}{T_0} - \frac{1}{T_1}\right]$$

extrapolating from -70 ^{o}C



(Table B.4.1) to T_{AVE} = -85 ^{o}C, $h_{FG} \approx 256.5$

Also $R = \frac{8.3145}{86.469} = 0.096\ 15$ kJ/kg K

For T_0 = 203.2 K & T_1 = 173.2 K

$$\ln\left(\frac{P_{G1}}{20.5}\right) = \frac{256.5}{0.096\ 15}\left[\frac{1}{203.2} - \frac{1}{173.2}\right]$$

P_{G1} = **2.107 kPa**

b) Extrapolating v_F from -70 ^{o}C to T_1 = -100 ^{o}C

$v_{F1} \approx 0.000\ 634$

Also $v_{G1} \approx RT_1/P_{G1} = \frac{0.096\ 15\times173.2}{2.107} = 7.9037$

Since $v_1 = v_2 \approx v_{F2} = 0.000\ 824$

$0.000\ 824 = 0.000\ 634 + x_1\times7.9031 \Rightarrow x_1 = 2.404\times10^{-5}$

$$\frac{V_{LIQ\ 1}}{m} = (1-x_1)v_{F1} = 0.000\ 634,\quad \frac{V_{VAP\ 1}}{m} = x_1 v_{G1} = 0.000\ 190$$

% LIQ, by vol. = $\frac{0.000\ 634}{0.000\ 824}\times100$ = **76.9 %**

13.114

The refrigerant R-152a, difluoroethane, is tested by the following procedure. A 10-L evacuated tank is connected to a line flowing saturated-vapor R-152a at 40°C. The valve is then opened, and the fluid flows in rapidly, so that the process is essentially adiabatic. The valve is to be closed when the pressure reaches a certain value P_2, and the tank will then be disconnected from the line. After a period of time, the temperature inside the tank will return to ambient temperature, 25°C, through heat transfer with the surroundings. At this time, the pressure inside the tank must be 500 kPa. What is the pressure P_2 at which the valve should be closed during the filling process? The ideal gas specific heat of R-152a is $C_{P0} = 0.996$ kJ/kg K.

R-152a CHF_2CH_3 : A.2: $M = 66.05$, $T_C = 386.4$ K, $P_C = 4.52$ MPa,

$T_3 = T_0 = 25^oC$, $P_3 = 500$ kPa, $R = \bar{R}/M = 8.3145/66.05 = 0.12588$

$T_{r3} = 298.2/386.4 = 0.772$, $P_{r3} = 500/4520 = 0.111$

From D.1 and D.2 at 3: $Z_3 = 0.92$, $(h^*\text{-}h)_3 = 0.19\ RT_C$

$$\Rightarrow \quad m_3 = m_2 = m_i = \frac{P_3V}{Z_3RT_3} = \frac{500\times0.010}{0.92\times0.125\ 88\times298.2} = 0.145 \text{ kg}$$

Filling process: Energy Eq.: $h_i = u_2 = h_2 - Z_2RT_2$

$$\text{or} \qquad (h_2\text{-}h_2^*) + C_{P0}(T_2\text{-}T_i) + (h_i^*\text{-}h_i) - P_2V/m_2 = 0$$

From D.2 with $T_{ri} = 313.2/386.4 = 0.811$,

$(h_i^*\text{-}h_i) = 0.125\ 88\times386.4\times0.49 = 23.8$; $P_i = 0.276\times4520 = 1248$ kPa

Assume $P_2 = 575$ kPa, $P_{r2} = 0.127$

Now assume $T_2 = 339$ K, $T_{r2} = 0.877$ => From D.1: $Z_2 = 0.93$

$$\Rightarrow \frac{Z_2T_2}{P_2} = \frac{0.93\times339}{575} = 0.5483 \approx \frac{Z_3T_3}{P_3} = \frac{0.92\times298.2}{500} = 0.5487$$

$\Rightarrow T_2 = 339$ K is the correct T_2 for the assumed P_2 of 575 kPa. Now check the 1st law to see if 575 kPa is the correct P_2.

From D.2, $h_2^*\text{-}h_2 = 0.125\ 88\times386.4\times0.17 = 8.3$

$$\text{Energy eq.:} \qquad -8.3 + 0.996(339\text{-}313.2) + 23.8 - \frac{575\times0.010}{0.1456} = +1.5 \approx 0$$

$\Rightarrow P_2 =$ **575 kPa**

(Note: for $P_2 = 580$ kPa, $T_2 = 342$ K, 1st law sum = +4.2)

13.115

Carbon dioxide gas enters a turbine at 5 MPa, 100°C, and exits at 1 MPa. If the isentropic efficiency of the turbine is 75%, determine the exit temperature and the second-law efficiency.

CO_2 turbine: $\eta_S = w/w_S = 0.75$

inlet: $T_1 = 100^oC$, $P_1 = 5$ MPa, exhaust: $P_2 = 1$ MPa

a) $P_{r1} = \frac{5}{7.38} = 0.678$, $T_{r1} = \frac{373.2}{304.1} = 1.227$, $P_{r2} = \frac{1}{7.38} = 0.136$

From D.2 and D.3,

$(h^*_1\text{-}h_1) = 0.188\ 92 \times 304.1 \times 0.52 = 29.9$

$(s^*_1\text{-}s_1) = 0.188\ 92 \times 0.30 = 0.0567$

Assume $T_{2S} = 253$ K, $T_{r2S} = 0.832$

From D.2 and D.3: $(h^*_{2S}\text{-}h_{2S}) = RT_C \times 0.20 = 11.5$

$(s^*_{2S}\text{-}s_{2S}) = R \times 0.17 = 0.0321$

$(s^*_{2S}\text{-}s^*_1) = 0.8418 \ln\frac{253}{373.2} - 0.188\ 92 \ln\frac{1}{5} = -0.0232$

$(s_{2S}\text{-}s_1) = -0.0321 - 0.0232 + 0.0567 \approx 0$

$\Rightarrow T_{2S} = 253$ K

$(h^*_{2S}\text{-}h^*_1) = 0.8418(253\text{-}373.2) = -101.2$

$w_S = (h_1\text{-}h_{2S}) = -29.9 + 101.2 + 11.5 = 82.8$ kJ/kg

$w = \eta_S \times w_S = 0.75 \times 82.8 = 62.1$ kJ/kg $= (h_1\text{-}h^*_1) + (h^*_1\text{-}h^*_2) + (h^*_2\text{-}h_2)$

Assume $T_2 = 275$ K, $T_{r2} = 0.904$

$(h^*_1\text{-}h^*_2) = 0.8418(373.2\text{-}275) = 82.7$

From D.2 and D.3,

$(h^*_2\text{-}h_2) = RT_C \times 0.17 = 9.8$; $(s^*_2\text{-}s_2) = R \times 0.13 = 0.0245$

Substituting,

$w = -29.9 + 82.7 + 9.8 = 62.7 \approx 62.1$ $\Rightarrow T_2 =$ **275 K**

b) $(s^*_2\text{-}s^*_1) = 0.8418 \ln\frac{275}{373.2} - 0.188\ 92 \ln\frac{1}{5} = +0.0470$

$(s_2-s_1) = -0.0245 + 0.0470 + 0.0567 = +0.0792$

Assuming $T_0 = 25\ ^oC$,

$(\varphi_1-\varphi_2) = (h_1 - h_2) - T_0(s_1 - s_2) = 62.1 + 298.2(0.0792) = 85.7$ kJ/kg

$$\eta_{2nd\ Law} = \frac{w}{\varphi_1-\varphi_2} = \frac{62.1}{85.7} = \mathbf{0.725}$$

13.116

A 4- m^3 uninsulated storage tank, initially evacuated, is connected to a line flowing ethane gas at 10 MPa, 100°C. The valve is opened, and ethane flows into the tank for a period of time, after which the valve is closed. Eventually, the whole system cools to ambient temperature, 0°C, at which time the it contains one-fourth liquid and three-fourths vapor, by volume. For the overall process, calculate the heat transfer from the tank and the net change of entropy.

Rigid tank $V = 4\ m^3$, $m_1 = 0$

Line: C_2H_6 at $P_i = 10$ MPa, $T_i = 100\ ^oC$

Flow in, then cool to $T_2 = T_0 = 0\ ^oC$, $V_{LIQ\,2} = 1\ m^3$ & $V_{VAP\,2} = 3\ m^3$

$M = 30.07$, $R = 0.2765$, $C_{P0} = 1.766$

$$P_{ri} = \frac{10}{4.88} = 2.049, \quad T_{ri} = \frac{373.2}{305.4} = 1.225$$

From D.2 and D.3,

$(h_i^*-h_i) = 0.2765\times305.4\times2.0 = 168.9$ and $(s_i^*-s_i) = 0.2765\times1.22 = 0.3373$

$$T_{r2} = \frac{273.2}{305.4} = 0.895$$

From D.1, D.2 and D.3, $P_2 = P_G = 0.51\times4880 = 2489$ kPa

sat. liq.: $Z_F = 0.087$; $(h^*-h_F) = RT_C\times4.09 = 345.4$; $(s^*-s_F) = R\times4.3 = 1.189$

sat. vap. : $Z_G = 0.68$; $(h^*-h_G) = RT_C\times0.87 = 73.5$; $(s^*-s_G) = R\times0.70 = 0.193$

$$m_{LIQ\,2} = \frac{2489\times1}{0.087\times0.2765\times273.2} = 378.7 \text{ kg}$$

$$m_{VAP\,2} = \frac{2489\times3}{0.68\times0.2765\times273.2} = 145.4 \text{ kg}$$

$$m_2 = 524.1 \text{ kg} \quad => \quad x_2 = \frac{145.4}{524.1} = 0.277$$

1st law:

$$Q_{CV} = m_2u_2 - m_ih_i = m_2(h_2-h_i) - P_2V = m_2\left[(h_2-h_2^*) + (h_2^*-h_i^*) + (h_i^*-h_i)\right] - P_2V$$

$(h_2^*-h_i^*) = 1.7662(0-100) = -176.6$

$(h_2^*-h_2) = (1-x_2)(h_2^*-h_{F2}) + x_2(h_2^*-h_{G2})$

$= 0.723 \times 345.4 + 0.277 \times 73.5 = 270.1$

$$Q_{CV} = 524.1\big[-270.1 - 176.6 + 168.9\big] - 2489 \times 4 \ = \mathbf{-155\ 551\ kJ}$$

$$\Delta S_{NET} = m_2(s_2 - s_i) - Q_{CV}/T_0$$

$$(s_2 - s_i) = (s_2 - s_2^*) + (s_2^* - s_i^*) + (s_i^* - s_i)$$

$$(s_2^* - s_i^*) = 1.7662 \ln\frac{273.2}{373.2} - 0.2765 \ln\frac{2.489}{10} = -0.1664$$

$$(s_2^* - s_2) = (1 - x_2)(s_2^* - s_{F2}) + x_2(s_2^* - s_{G2})$$

$$= 0.723 \times 1.189 + 0.277 \times 0.193 = 0.9131$$

$$(s_2 - s_i) = -0.9131 - 0.1664 + 0.3373 = -0.7422$$

$$\Delta S_{NET} = 524.1(-0.7422) - \frac{-155\ 551}{273.2} = \mathbf{180.4\ kJ/K}$$

13.117

A 10- m^3 storage tank contains methane at low temperature. The pressure inside is 700 kPa, and the tank contains 25% liquid and 75% vapor, on a volume basis. The tank warms very slowly because heat is transferred from the ambient.

a. What is the temperature of the methane when the pressure reaches 10 MPa?

b. Calculate the heat transferred in the process, using the generalized charts.

c. Repeat parts (a) and (b), using the methane tables, Table B.7. Discuss the differences in the results.

CH_4: $V = 10\ m^3$, $P_1 = 700$ kPa

$V_{LIQ\ 1} = 2.5\ m^3$, $V_{VAP\ 1} = 7.5\ m^3$

a) $P_{r1} = \dfrac{0.70}{4.60} = 0.152,\ \ P_{r2} = \dfrac{10}{4.60} = 2.174$

From D.1: $Z_{F1} = 0.025$, $Z_{G1} = 0.87$ &

$T_1 = 0.74 \times 190.4 = 140.9$ K

$$v_{F1} = \frac{0.025\times0.518\ 35\times140.9}{700} = 0.00261$$

$$v_{G1} = \frac{0.87\times0.518\ 35\times140.9}{700} = 0.0908$$

$$m_{LIQ\ 1} = \frac{2.5}{0.00261} = 957.9\text{ kg},\ m_{VAP\ 1} = \frac{7.5}{0.0908} = 82.6\text{ kg}$$

Total m = 1040.3 kg

$$v_2 = v_1 = \frac{V}{m} = \frac{10}{1040.5} = 0.00961\ = \frac{Z_2\times0.518\ 35\times190.4\times T_{r2}}{10\ 000}$$

or $Z_2T_{r2} = 0.9737$ at $P_{r2} = 2.174$

By trial and error

$T_{r2} = 1.334$ & $Z_2 = 0.73$, $T_2\ = 1.334\times190.4 =$ **254.0 K**

b) 1st law:

$$Q_{12} = m(u_2\text{-}u_1) = m(h_2\text{-}h_1) - V(P_2\text{-}P_1)$$

$$\text{Using D.2 \& } x_1 = \frac{82.6}{1040.5} = 0.0794$$

$$(h^*_1\text{-}h_1) = (h^*_1\text{-}h_{F1}) - x_1h_{FG1}$$

$= 0.518\ 35 \times 190.4 \Big[4.72\text{-}0.0794(4.72\text{-}0.29) \Big] = 431.1$

$(h^*_2\text{-}h^*_1) = 2.2537(254.0\text{-}140.9) = 254.9$

$(h^*_2\text{-}h_2) = 0.518\ 35 \times 190.4(1.47) = 145.1$

$(h_2\text{-}h_1) = -145.1 + 254.9 + 431.1 = 540.9$ kJ/kg

$Q_{12} = 1040.5(540.9) - 10(10\ 000\text{-}700)$ = **469 806 kJ**

c) Using Table B.7 for CH_4

$T_1 = T_{SAT\ 1} = 141.7$ K, $v_{F1} = 0.002\ 675$, $u_{F1} = -178.47$

$v_{G1} = 0.090\ 45$, $u_{G1} = 199.84$

$$m_{LIQ\ 1} = \frac{2.5}{0.002\ 675} = 934.6,\ m_{VAP\ 1} = \frac{7.5}{0.090\ 45} = 82.9$$

$$\text{Total mass} \quad m = 1017.5 \text{ kg} \quad \text{and} \quad v_2 = \frac{10}{1017.5} = 0.009\ 828 \text{ m}^3\text{/kg}$$

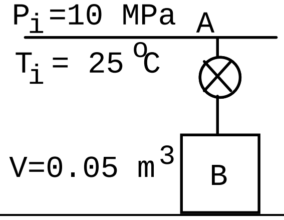
$$\text{At } v_2 \ \&\ P_2 = 10 \text{ MPa} \rightarrow \begin{cases} T_2 = 259.1 \text{ K} \\ u_2 = 296.11 \end{cases}$$

$Q_{12} = m(u_2\text{-}u_1) = 1017.5 \times 296.11 - 934.6(-178.47) - 82.9(199.84)$

= **451 523 kJ**

13.118

A gas mixture of a known composition is frequently required for different purposes, e.g., in the calibration of gas analyzers. It is desired to prepare a gas mixture of 80% ethylene and 20% carbon dioxide (mole basis) at 10 MPa, 25°C in an uninsulated, rigid 50-L tank. The tank is initially to contain CO2 at 25°C and some pressure *P*1. The valve to a line flowing C2H4 at 25°C, 10 MPa, is now opened slightly, and remains open until the tank reaches 10 MPa, at which point the temperature can be assumed to be 25°C. Assume that the gas mixture so prepared can be represented by Kay's rule and the generalized charts. Given the desired final state, what is the initial pressure of the carbon dioxide, *P*1?

	$A = C_2H_4$, $B = CO_2$ $T_1 = 25\ ^oC$ $P_2 = 10$ MPa, $T_2 = 25\ ^oC$ $y_{A2} = 0.8$, $y_{B2} = 0.2$	

Mixture at 2 :

$$P_{C2} = 0.8 \times 5.04 + 0.2 \times 7.38 = 5.508 \text{ MPa}$$

$$T_{C2} = 0.8 \times 282.4 + 0.2 \times 304.1 = 286.7 \text{ K}$$

$$T_{r2} = 298.15/286.7 = 1.040; \; P_{r2} = 10/5.508 = 1.816$$

$$\text{D.1 :} \quad Z_2 = 0.32$$

$$n_2 = \frac{P_2V}{Z_2\bar{R}T_2} = \frac{10\,000 \times 0.05}{0.32 \times 8.3145 \times 298.2} = 0.6302 \text{ kmol}$$

$$n_{A2} = n_i = 0.8\ n_2 = 0.5042 \text{ kmol } C_2H_4$$

$$n_{B2} = n_1 = 0.2\ n_2 = 0.1260 \text{ kmol } CO_2$$

$$T_{r1} = \frac{298.2}{304.1} = 0.981$$

$$P_{r1} = \frac{n_1Z_{B1}\bar{R}T_1}{P_{CB}V} = \frac{0.126\ Z_{B1} \times 8.3145 \times 298.2}{7380 \times 0.05} = 0.8466\ Z_{B1}$$

By trial & error: $P_{r1} = 0.618$ & $Z_{B1} = 0.73$

$\Rightarrow P_1 = 0.618 \times 7.38 =$ **4.56 MPa**

13.119

Determine the heat transfer and the net entropy change in the previous problem. Use the initial pressure of the carbon dioxide to be 4.56 MPa before the ethylene is flowing into the tank.

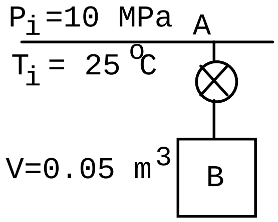
A gas mixture of a known composition is frequently required for different purposes, e.g., in the calibration of gas analyzers. It is desired to prepare a gas mixture of 80% ethylene and 20% carbon dioxide (mole basis) at 10 MPa, 25°C in an uninsulated, rigid 50-L tank. The tank is initially to contain CO2 at 25°C and some pressure *P*1. The valve to a line flowing C2H4 at 25°C, 10 MPa, is now opened slightly, and remains open until the tank reaches 10 MPa, at which point the temperature can be assumed to be 25°C. Assume that the gas mixture so prepared can be represented by Kay's rule and the generalized charts. Given the desired final state, what is the initial pressure of the carbon dioxide, *P*1?

$A = C_2H_4$, $B = CO_2$

$T_1 = 25\ ^oC$

$P_2 = 10$ MPa, $T_2 = 25\ ^oC$

$y_{A2} = 0.8$, $y_{B2} = 0.2$



Mixture at 2 :

$P_{C2} = 0.8 \times 5.04 + 0.2 \times 7.38 = 5.508$ MPa

$T_{C2} = 0.8 \times 282.4 + 0.2 \times 304.1 = 286.7$ K

$T_{r2} = 298.15/286.7 = 1.040$; $P_{r2} = 10/5.508 = 1.816$

D.1 : $Z_2 = 0.32$

$$n_2 = \frac{P_2V}{Z_2\bar{R}T_2} = \frac{10\,000\times0.05}{0.32\times8.3145\times298.2} = 0.6302 \text{ kmol}$$

$n_{A2} = n_i = 0.8\ n_2 = 0.5042$ kmol C_2H_4

$n_{B2} = n_1 = 0.2\ n_2 = 0.1260$ kmol CO_2

$$T_{r1} = \frac{298.2}{304.1} = 0.981 \text{ and } P_{r1} = \frac{4560}{7380} = 0.618$$

1st law: $Q_{CV} + n_i\bar{h}_i = n_2\bar{u}_2 - n_1\bar{u}_1 = n_2\bar{h}_2 - n_1\bar{h}_1 - (P_2-P_1)V$

or $Q_{CV} = n_2(\bar{h}_2-\bar{h}_2^*) - n_1(\bar{h}_1-\bar{h}_1^*) - n_i(\bar{h}_i-\bar{h}_i^*) - (P_2-P_1)V$

(since $T_i = T_1 = T_2$, $\bar{h}_i^* = \bar{h}_1^* = \bar{h}_2^*$)

$(\bar{h}_1^* - \bar{h}_1) = 0.83 \times 8.3145 \times 304.1 = 2099$ kJ/kmol

$(\bar{h}_2^* - \bar{h}_2) = 3.40 \times 8.3145 \times 286.7 = 8105$ kJ/kmol

$T_{ri} = \dfrac{298.2}{282.4} = 1.056,\ P_{ri} = \dfrac{10}{5.04} = 1.984$

$(\bar{h}_i^* - \bar{h}_i) = 3.35 \times 8.3145 \times 282.4 = 7866$ kJ/kmol

$Q_{CV} = 0.6302(-8105) - 0.126(-2099) - 0.5042(-7866) - (10\ 000 - 4560) \times 0.05$

$= \mathbf{-1149\ kJ}$

$\Delta S_{CV} = n_2\bar{s}_2 - n_1\bar{s}_1\ ,\quad \Delta S_{SURR} = - Q_{CV}/T_0 - n_i\bar{s}_i$

$\Delta S_{NET} = n_2\bar{s}_2 - n_1\bar{s}_1 - Q_{CV}/T_0 - n_i\bar{s}_i$

Let $\bar{s}^*_{A0} = \bar{s}^*_{B0} = 0$ at $T_0 = 25\ ^oC$, $P_0 = 0.1$ MPa

Then $\bar{s}^*_{MIX\ 0} = -8.3145\ (0.8 \ln 0.8 + 0.2 \ln 0.2) = 4.161$ kJ/kmol K

$\bar{s}_1 = \bar{s}^*_{B0} + (\bar{s}^*_{P1\ T1} - \bar{s}^*_{P0\ T0})_B + (\bar{s}_1 - \bar{s}^*_{P1\ T1})_B$

$= 0 + (0 - 8.3145 \ln \dfrac{4.56}{0.1}) - 0.60 \times 8.3145 = -36.75$ kJ/kmol K

$\bar{s}_i = \bar{s}^*_{A0} + (\bar{s}^*_{Pi\ Ti} - \bar{s}^*_{P0\ T0})_A + (\bar{s}_i - \bar{s}^*_{Pi\ Ti})_A$

$= 0 + (0 - 8.3145 \ln \dfrac{10}{0.1}) - 2.44 \times 8.3145 = -58.58$ kJ/kmol K

$\bar{s}_2 = \bar{s}^*_{MIX\ 0} + (\bar{s}^*_{P2\ T2} - \bar{s}^*_{P0\ T0})_{MIX} + (\bar{s}_2 - \bar{s}^*_{P2\ T2})_{MIX}$

$= 4.161 + (0 - 8.3145 \ln \dfrac{10}{0.1}) - 2.551 \times 8.3145 = -55.34$ kJ/kmol K

$\Delta S_{NET} = 0.6302(-55.33) - 0.126(-36.75) - 0.5042(-58.58) + 1149/298.2$

$= \mathbf{+3.15\ kJ/K}$