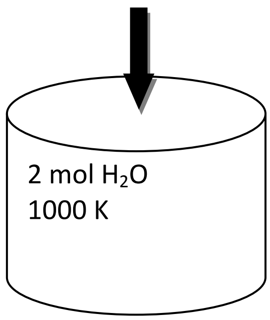
Problem Set 4
10.213 Chemical and Biological Thermodynamics
Solution to Problem 4.19



A cylinder containing water vapor is compressed reversibly from 10 L to 1 L. Calculate the amount of work required using different gas models and the steam tables.

a. Ideal Gas Model

- PV=nRT
- The gas is a closed system with one moving boundary.
- T=1000 K
- n= 2 mol

$$W = \int_{V_{1g}}^{V_{2g}} -P dV_g \qquad \text{[1 point]}$$

$$W = -\int_{V_{1g}}^{V_{2g}} \frac{nRT}{V_g} dV_g$$

$$W = -nRT \int_{10L}^{1L} \left(\frac{1}{V_g}\right) dV_g \qquad \text{[1 point]}$$

$$W = -2mol * 8.31447 \frac{J}{molK} * 1000K * \ln\left(\frac{1}{10}\right)$$

$$W = 38.3\, kJ \qquad \text{[1 point]}$$

b. Redlich-Kwong equation

- $P = \dfrac{RT}{V-b} - \dfrac{a}{T^{1/2}V(V+b)}$
- $a = 14.24[(JK^{1/2}m^3)/mol^2], \quad b = 2.11*10^{-5}[m^3/mol]$
- Volume in State 1: V_1=10L = 10^{-2} m^3
- Volume in State 2: V_2= 1 L = 10^{-3} m^3
- Be careful to convert the R-K equation to total volume basis!

$$W = \int_{V1}^{V2} -PdV_g$$

$$W = -\int_{V1}^{V2} \frac{nRT}{V_g - nb} - \frac{an^2}{T^{1/2}V_g(V_g + nb)} dV_g \qquad \text{[1 point]}$$

$$W = -nRT\ln(V_g - nb) + \frac{an}{T^{1/2}b}\ln\left(\frac{V}{V+nb}\right)\Bigg|_{10^{-2}m^3}^{10^{-3}m^3}$$

$$W = -2mol * 8.31447\frac{J}{molK} * 1000K\ln\left(\frac{10^{-3}m^3 - 2mol * 2.11 * 10\wedge -5\frac{m^3}{mol}}{10^{-2}m^3 - 2mol * 2.11 * 10\wedge -5\frac{m^3}{mol}}\right) +$$

$$\frac{14.24\frac{JK^{1/2}m^3}{mol^2} * 2mol}{(1000K)^{1/2} * 2.11 * 10^{-5}\frac{m^3}{mol}}\left[\ln\left(\frac{10^{-3}m^3}{10^{-3}m^3 + 2mol * 2.11 * 10^{-5}\frac{m^3}{mol}}\right) - \ln\left(\frac{10^{-2}m^3}{(10^{-2}m^3 + 2mol * 2.11 * 10^{-5}\frac{m^3}{mol}}\right)\right]$$

$$W = 37.35\,kW \qquad \text{[2 point]}$$

c. Steam Tables

Perform an energy balance on the compression of the gas:

- Assume KE and PE changes are negligible
- Isothermal process, so $\Delta U=0$

Thus the energy balance simplifies to $W_{rev}=-Q_{rev}$ [1 point]

Because the process is reversible, the amount of heat loss is equal to $Q_{rev}=T\Delta S$. [1 point]
To determine the entropy of the system in the initial and final states, we use the temperature and molar volume of the gas. In the initial state, the molar volume is 10 L/2 mol= 5 L/mol while in the final state it is 1 L/2 mol = 0.5 L/mol. Combining this with the temperature of 1000 K, we find using the NIST database the entropies of water in the initial and final states:

s_1=145.97 J/mol K
s_2=125.99 J/mol K

Now we can calculate the amount of heat loss and the work performed.

Q_{rev}= $nT\Delta s$
= 2 mol * 1000K*(125.99 J/mol K-145.97 J/mol K)
= -39.96 kJ
W_{rev}= -Q_{rev}= + **39.96 kJ** [2 point]

In this case, the ideal gas model was the better predictor of fluid behavior.

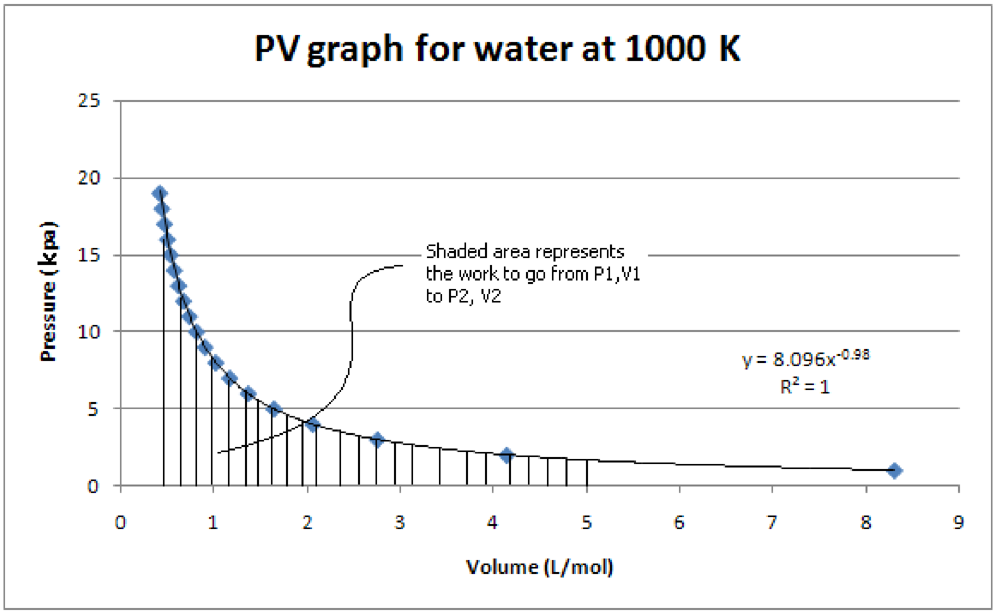
Method 2: Use the Steam Tables to estimate a P-V relationship for water at 1000 K

From webbook.nist.gov,

Table 1: Fluid data for water at 1000 K

Pressure (kPa)	Volume (m3/kg)
1	8.2932
2	4.1359
3	2.7502
4	2.0573
5	1.6416
6	1.3644
7	1.1664
8	1.0179
9	0.90241
10	0.81002
11	0.73442
12	0.67142
13	0.61811
14	0.5724
15	0.53282
16	0.49817
17	0.4676
18	0.44043
19	0.41612
20	0.39424

The amount of work required to compress the gas isothermally is equivalent to the area underneath a P vs. V graph, from 0.5 L/mol to 5 L/mol.



$$W = \int_{V1}^{V2} -PdV_g$$

$$W = \int_{10L}^{1L} -\frac{n^{0.98} * 8.096}{V_g^{\ 0.98}} dV_g$$

$$W = 37.6\,kW$$

Grading Scheme for method 2:

1 point for Equation of curve fit to appropriate data

1 point for integration of P-V data

2 points for W = 37.6 kW