

CYL100 2013–14 I semester Homework 2 Solutions

1. Consider a well-insulated piston-cylinder assembly. On the 0.05 m^2 piston rests two 5000-kg blocks. The initial temperature is 500 K. The ambient pressure is 5 bar. One mole of an ideal gas is contained in the cylinder. The gas is compressed in a process in which another 5000-kg block is added. The heat capacity at constant volume can be taken to have a constant value of $(5/2)R$.

- (a) What are the initial and final pressures of the gas in the system?

$$P_1 = P_{surr} + \frac{2(5000\text{kg})(9.81\text{m/s}^2)}{0.05\text{m}^2} = 24.6 \times 10^5 \text{ Pa}$$

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- (b) Do you expect the temperature to rise or fall? Explain.

Temperature should rise - convention we have followed is that work done on the system is positive. System is insulated so energy conservation would require the temperature to rise.

- (c) What is the final temperature?

$$\Delta U = w; nC_v(T_2 - T_1) = -P_2(V_2 - V_1)$$

$$n(5/2R)(T_2 - T_1) = -P_2\left(\frac{nRT_2}{P_2} - V_1\right); T_2 = 557\text{K}$$

- (d) Calculate ΔS_{sys} and ΔS_{surr} .

$$\Delta S_{surr} = 0; \Delta S_{sys} = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} = 0.354 \text{ J/molK}$$

- (e) Does this process violate the second law of thermodynamics? Explain.

No. $\Delta S_{total} = \Delta S_{sys} > 0$.

2. For the process given in the problem above, calculate ΔS_{sys} using each of the following paths:

Without calculation we know that we should get the same result as above for these three paths between the same initial and final state.

- (a) a reversible, adiabatic compression, followed by a reversible, isothermal expansion

$$(P_i, T_i) = (24.6\text{bar}, 500\text{K}) \rightarrow (P_2, T_f) = (P_2, 557\text{K}) \rightarrow (P_f, T_f) = (34.4\text{bar}, 557\text{K})$$

Entropy in the first step is zero - adiabatic reversible compression.

$$P_2 = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma}{\gamma-1}} P_i = 35.9\text{bar}$$

$$\Delta S = -R \ln P_2/P_1$$

- (b) a reversible, isobaric heating followed by a reversible, isothermal compression

$$(P_i, T_i) = (24.6\text{bar}, 500\text{K}) \rightarrow (24.6\text{bar}, 557\text{K}) \rightarrow (P_f, T_f) = (34.4\text{bar}, 557\text{K})$$

Entropy change during a reversible, isobaric heating is $\Delta S = C_P \ln T_f/T_i$ while it is $\Delta S = -R \ln P_f/P_i = R \ln V_i/V_f$ during a reversible isothermal compression.

- (c) a reversible, isochoric heating followed by a reversible, isothermal compression

$$(P_i, T_i) = (24.6\text{bar}, 500\text{K}) \rightarrow (P_2, T_f) = (P_2, 557\text{K}) \rightarrow (P_f, T_f) = (34.4\text{bar}, 557\text{K})$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Entropy change during a reversible, isochoric heating is $\Delta S = C_v \ln T_f/T_i$ while it is $\Delta S = -R \ln P_f/P_2 = R \ln T_f/T_i - R \ln P_f/P_i$ during a reversible isothermal compression.

3. A salesperson claims that a mysterious black box, with no moving parts, can take an inlet stream of ideal gas at 2 kg/s and 4 bar and 50 °C and cool 0.5 kg/s of it to -10 °C and 1 bar while the rest of the gas is raised to 70 °C at 1 bar. Is this possible? Explain.

(i) Mass is conserved

(ii) Energy is conserved: $0.5kg/sC_P(-10 - 50)K = 1.5kg/sC_P(70 - 50)K$

(iii) Does the second law hold? For an adiabatic process,

$$\frac{dS}{dt}_{univ} = 0.5kg/s(S_2 - S_1) + 1.5kg/s(S_3 - S_1)$$

$$S_2 - S_1 = C_p \ln T_2/T_1 - R \ln P_2/P_1$$

$$S_3 - S_1 = C_p \ln T_3/T_1 - R \ln P_3/P_1$$

$$\frac{dS}{dt}_{univ} = 0.5kg/sC_P(\ln 263 + 3 \ln 343 - 4 \ln 323) + 2R \ln 4$$

Second law holds as long as $C_P \leq 218R$, which is true for all imaginable gases.

4. Calculate the maximum work and the maximum non-expansion work that can be obtained from the freezing of supercooled water at -5 °C and 1.0 atm. The densities of water and ice are 0.999 and 0.917 g cm⁻³, respectively at -5 °C.

The simplest procedure is to calculate the change in G and A by using the relationship $\Delta A = \Delta U - T\Delta S$ and $\Delta G = \Delta H - T\Delta S$. From thermodynamic tables we know that $\Delta H = -6008$ J/mol for freezing at 0 °C, C_P for liquid water is 75 J/(mol K), and C_P for ice is 36.4 J/(mol K). The computation of ΔH and ΔS was discussed in class. As a zeroth approximation, we could take that $\Delta U = \Delta H$ because condensed phases are involved. We could do better by using the densities to find the PdV contribution to ΔH .

$$\Delta H(268K) = \Delta H(273K) + (C_P(solid) - C_P(liquid))(-5K)$$

$$\Delta U(268K) = \Delta H(268K) - 1atm(V_m(solid) - V_m(liquid))$$

$$\Delta S(268K)$$

5. One mole of He is heated from 200 °C to 400 °C at a constant pressure of 1 atm. Given that the absolute entropy of He at 200 °C is 810 JK⁻¹ mol⁻¹, and assuming He is a perfect gas, comment on the spontaneity of the process.

$$\Delta S = S_0 + C_P \ln 673/473$$

The spontaneity of the process will be determined by how the heating is done. If the heating is achieved by putting the gas into a heat bath at 400 °C, then $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} > 0$.

$$\Delta S_{surr} = -\Delta H_{sys}/673; \quad \Delta H_{sys} = C_P(200K)$$

6. Derive the relations: (i) $C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$;

$$\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

Use the definition $H = U + PV$

$$\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

To obtain an expression for $\left(\frac{\partial U}{\partial T}\right)_P$ we proceed as follows

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Dividing by dT and applying constant pressure gives

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Thus we have

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

Using the result that was proved in class

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

yields what we set out to prove.

$$(ii) C_p - C_v = \frac{\alpha^2 TV}{\beta}$$

After all the effort of the previous part, this is straightforward. Use the definition of $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ and $\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ and the cyclic relation $\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -1$ in the result that was derived in part (i).

$$(iii) \mu_{JT} = -(V/C_p)(\beta C_v \mu_J - \beta P + 1)$$

The toughest part is to look up the definitions of μ_{JT} and μ_J . $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$ and $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$

$$(iv) \left(\frac{\partial H}{\partial V}\right)_S = \gamma/\beta$$

This is a slightly tricky one. We first use the relation

$$\left(\frac{\partial H}{\partial V}\right)_S = \left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial P}{\partial V}\right)_S$$

From the relation $dH = TdS + VdP$ we know that

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

Use the cyclic relation to write

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{1}{\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_V}$$

Now rewrite

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P$$

and

$$\left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$$

Use the fact that

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$$

and

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{C_V}{T} \\ \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_P &= -\left(\frac{\partial V}{\partial P}\right)_T \end{aligned}$$

to obtain the stated relation.

$$(v) \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_V \beta}{T \alpha}$$

This looks suspicious. My guess is that it is wrong. The dimensions on both sides seem to match. The left hand side is $V\alpha$ implying that $C_V = \frac{TV\alpha^2}{\beta}$. This cannot be correct because in part (ii) we proved that this quantity is $C_P - C_V$. Oops! Sorry!

7. (a) Calculate the change in the chemical potential of a perfect gas when its pressure is increased isothermally from 1.8 atm to 29.5 atm at 40 °C.

$$\Delta\mu = RT \ln \frac{P_2}{P_1}$$

(b) The molar Gibbs energy of a certain gas is given by

$$G_m = RT \ln p + A + Bp + \frac{1}{2}Cp^2 + \frac{1}{3}Dp^3$$

where A, B, C, D are constants. Obtain the equation of state of the gas.

$$V_m = \left(\frac{\partial G}{\partial P}\right)_T = \frac{RT}{P} + B + CP + DP^2$$

8. At 1 atm the $S_{rh} \rightarrow S_{mon}$ transition takes place at 95.5 °C, and the melting point of S_{mon} is 119.3 °C. The latent heat of the rhombic to monoclinic transition is 1.1610^4 J kg⁻¹ and the latent heat of fusion of S_{mon} is 5.53×10^4 J kg⁻¹. The densities of rhombic, monoclinic, and liquid sulphur are 2.07×10^3 , 1.96×10^3 , 1.90×10^3 kg m⁻³. Estimate the rhombic, monoclinic, and liquid triple point.

Use the Clapeyron equation to determine the slopes of the two lines. We also know that the rhombic to monoclinic line passes through (95.5 °C, 1 atm). Similarly for the monoclinic melting. The intersection of these two lines gives the triple point.

9. The vapor pressure of zinc varies with temperature as

$$\log p(\text{mmHg}) = -\frac{6850}{T} - 0.755 \log T + 11.24$$

and that of liquid zinc as

$$\log p(\text{mmHg}) = -\frac{6620}{T} - 1.255 \log T + 12.34.$$

Calculate (a) the boiling point of zinc

At the boiling point, the vapor pressure of the liquid becomes the atmospheric pressure, which is 760 mm of Hg.

$$\log 760 = -\frac{6620}{T} - 1.255 \log T + 12.34$$

We solve this by the method of successive approximation. I drop the $\log T$ term to begin with and solve for T . This gives me an initial guess for the root to be $T = 699.85$. I use this guess root in the $\log T$ and solve the equation

$$\log 760 = -\frac{6620}{T} - 1.255 \log 699.85 + 12.34$$

for T , which yields $T = 1124.1$. I repeat this process a few times and find that $T = 1181$.

There are other methods to solve this - graphical and using a computer algebra system are two possibilities.

(b) the triple point

At the triple point, the solid-vapor and liquid-vapor coexistence curves intersect. This means

$$-\frac{6620}{T} - 1.255 \log T + 12.34 = -\frac{6850}{T} - 0.755 \log T + 11.24$$

$$\frac{230}{T} - 0.5 \log T + 1.10 = 0$$

Solving this equation we find that the temperature at the triple point is close to 700. One uses this T in one of the equations to find the P .

(c) the heat of evaporation at the boiling point

$$2.303 \log p(\text{mmHg}) = \ln P = 2.303 \left(-\frac{6620}{T} - 1.255 \log T + 12.34 \right)$$

$$d \ln P = 2.303 R dT \left(\frac{6620}{RT^2} - \frac{1.255}{RT} \right) = 2.303 R \frac{6620 - 1.255T}{RT^2} dT$$

Comparing this with the Clausius-Clapeyron equation, $d \ln P = \Delta H^\circ / RT^2 dT$, shows that $\Delta H^\circ = 2.303R(6620 - 1.255T)$. Substitute the boiling point $T = 1181$ in $\Delta H^\circ = 2.303R(6620 - 1.255T)$ and obtain ΔH° .

(d) the heat of fusion

The heat of fusion, which is the enthalpy of melting, may be obtained from subtracting the heat of evaporation from the heat of sublimation. The heat of sublimation is obtained by following the same procedure as in part (c) for the sublimation curve.

(e) the difference in the C_p s of solid and liquid zinc.

If ΔH° has the form $A + BT$, then it implies that $B = C_P$. From the temperature dependent part of ΔH° for evaporation and sublimation, we can obtain the difference in the C_P 's.

10. The Planck function defined as

$$Y = -\frac{H}{T} + S$$

is a thermodynamic potential similar to the Gibbs energy. Obtain a " TdS " type equation for dY and from it a Maxwell relation. Also, what is the thermodynamic criterion for spontaneity in terms of Y .

$$dY = \frac{H}{T^2} dT - \frac{dH}{T} + dS = \frac{H}{T^2} dT - \frac{1}{T} (dH - TdS)$$

We know that $dH = TdS - VdP$ so that

$$dY = \frac{H}{T^2} dT - \frac{V}{T} dP$$

Comparing this with

$$dY = \left(\frac{\partial Y}{\partial T} \right)_P dT + \left(\frac{\partial Y}{\partial P} \right)_T dP$$

suggests that

$$\left(\frac{\partial Y}{\partial T}\right)_P = \frac{H}{T^2} \quad \text{and} \quad \left(\frac{\partial Y}{\partial P}\right)_T = -\frac{V}{T}.$$

Because Y is a state function, we know

$$\begin{aligned} \left(\frac{\partial^2 Y}{\partial P \partial T}\right) &= \left(\frac{\partial^2 Y}{\partial T \partial P}\right) \\ \left(\frac{\partial}{\partial P} \frac{H}{T^2}\right) &= \left(\frac{\partial}{\partial T} \frac{V}{T}\right) \\ \frac{1}{T^2} \left(\frac{\partial H}{\partial P}\right)_T &= \frac{V}{T^2} - \frac{1}{T} \left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial H}{\partial P}\right)_T &= V - T \left(\frac{\partial V}{\partial T}\right)_P, \end{aligned}$$

which is a result we derived earlier by another approach.

We see that $Y = -\frac{G}{T}$, which suggests that $(dY)_{T,P} \geq 0$ would be the condition for spontaneity and equilibrium.

11. It is often claimed that one can skate on ice because the pressure of the skate causes the ice to melt, thus dramatically reducing the friction between skate and ice. While this makes a good story, is this quite correct? Consider a skater with a mass of 75 kg on a skate that is 3 mm wide and 20 cm long. The densities of water and ice are 0.999 and 0.917 g cm⁻³ respectively, and the heat of fusion is 6.004 kJ mol⁻¹. Since common experience is that ice skating is possible even when the ambient temperature is well below the normal freezing point, does the pressure induced lowering of the melting point explain clearly this observation?

Straightforward implementation of the Clapeyron equation (watch out for the units and remember that we need the molar volume) using the data given

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} = \frac{6004}{2730.018 \left(\frac{1}{999} - \frac{1}{917}\right)} = 1.3649 \times 10^7 Pa$$

shows that it requires more than 130 atm to decrease the melting point by 1 K at 273K. The pressure exerted by the skater is a little over an atmosphere so that the change in melting point as a result of the pressure on the skates is at most a few hundredths of a degree. The pressure induced lowering of the melting point clearly does not explain this every day observation.