Exam T6

Thermodynamics and Statistical Physics 2018-2019

Tuesday, January 22, 2019, 9:00-12:00

Read these instructions carefully before making the exam!

- **Write your name and student number on *every* sheet.**
- *Make sure to write readable for other people than yourself. Points will NOT be given for answers in illegible writing.*
- *Language*; **your answers have to be in English.**
- **Use a *separate* sheet for each problem.**
- **Use of a (graphing) calculator is allowed.**
- **This exam consists of 4 problems.**
- **The weight of the problems is Problem 1 (P1=25 pts); Problem 2 (P2=20 pts); Problem 3 (P3=25 pts) and Problem 4 (P4=20 pts). Weights of the various subproblems are indicated at the beginning of each problem.**
- **The grade of the exam is calculated as (P1+P2+P3 +P4+10)/10.**
- **For all problems you have to write down your arguments and the intermediate steps in your calculation,** *else the answer will be considered as incomplete and points will be deducted.*

PROBLEM 1 Name S-number		PROBLEM 2 Name S-number		PROBLEM 3 Name S-number		PROBLEM 4 Name S-number	

PROBLEM 1
Score: a+b+c+d+e+f=4+4+5+4+4+4=25

The van der Waals equation of state for a real gas is:

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

in which P, V, T are the pressure, the *molar* volume and the temperature of the gas, respectively. The positive constant a controls the attractive molecular interactions and the positive constant b corrects for the volume of the gas molecules.

a) Consider the gas molecules to be hard spheres with radius r. Derive an approximate expression for the constant b in terms of r.

b) Qualitatively derive the second term $\left(-\frac{a}{V^2}\right)$ that accounts for the attractive molecular forces.

c) Calculate the temperature, pressure and volume of a van der Waals gas at the critical point. Express your answer in terms of a, b and R.

d) Make a sketch of a PV-diagram with the critical isotherm of a van der Waals gas. Also sketch in this diagram an isotherm for $T > T_c$ and one for $T < T_c$ (T_c is the critical temperature).

e) Use the fact that $F = U - TS$ is an exact differential to show that:

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

and use this equation and the first law to show that for an isothermal expansion of a gas we have:

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

f) Calculate the change in the internal energy ΔU and in the entropy ΔS during an isothermal free expansion (from volume V_0 to volume $2V_0$) of a van der Waals gas. Are these changes in internal energy and entropy, zero, positive or negative? Explain why?

PROBLEM 2
Score: a+b+c+d+e=3+5+5+4+3=20

In the Joule-Kelvin expansion a steady flow of a gas at a high pressure p_1 is forced through a porous plug (throttle) to a lower pressure p_2.
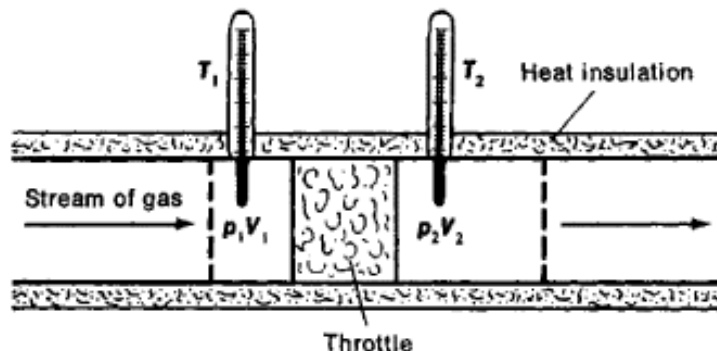
a) Explain why the enthalpy H of the gas does not change in the Joule-Kelvin expansion.

The Joule-Kelvin coefficient describes the change in temperature T of the gas when the pressure p of the gas is reduced at constant enthalpy,

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H$$

b) Show that μ_{JK} can be written as:

$$\mu_{JK} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

with C_p the heat capacity at constant pressure of the gas.

HINTS: use that the enthalpy H is an exact differential and use the Maxwell relation: $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$.

For a *dilute* real gas the equation of state can be approximated by:

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V}$$

with $B(T)$ the second virial coefficient and V the molar volume.

c) Show that when $\left|\frac{B(T)}{V}\right| \ll 1$ the Joule-Kelvin coefficient can be written as:

$$\mu_{JK} = \frac{1}{C_p}\left(T\frac{\partial B(T)}{\partial T} - B(T)\right)$$

Continued on next page.

PROBLEM 2 (cont.)

d) Show that the Joule-Kelvin coefficient for a dilute van der Waals gas is given by (hint: the van der Waals equation of state is given in problem 1):

$$\mu_{JK} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

e) Discuss if a dilute van der Waals gas will be cooled or heated by the Joule-Kelvin process in case of very low temperatures, and in case of very high temperatures.

PROBLEM 3
Score: a+b+c+d+e=5+5+5+5+5=25

Consider a three-dimensional non-relativistic ideal gas of N fermions with mass m and spin S that is confined to a volume V and is in equilibrium with a heat bath at temperature T and a particle reservoir with chemical potential μ.

HINT 1: The density of states for a *spinless* particle confined to an enclosure with volume V is (expressed as a function of the particle's momentum p):

$$g(p)dp = \frac{V}{h^3} 4\pi p^2 dp$$

HINT 2: For fermions the mean occupation of a single-particle state with energy E is given by:

$$f(E) = \frac{1}{e^{\beta(E-\mu)} + 1}$$

a) Show that for this gas the density of states can be expressed in term of energy as:

$$g(E)dE = \frac{V(2S+1)}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{E} dE$$

b) Give the definition of the Fermi energy E_F and sketch the function $f(E)$ from HINT 2 at $T = 0$. Use E/E_F for the horizontal axis of the sketch. Give arguments for the shape of your sketch.

c) Show that the Fermi energy E_F of this gas is,

$$E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{2S+1} \frac{N}{V}\right)^{\frac{2}{3}}$$

d) Show that the total energy U of this gas at $T = 0$ is:

$$U = \frac{3}{5} \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{2S+1}\right)^{\frac{2}{3}} \frac{N^{\frac{5}{3}}}{V^{\frac{2}{3}}}$$

PROBLEM 3 (cont.)

e) A system consists of a sliding piston that separates two compartments of a container. Compartment 1 contains spin 1/2 particles and compartment 2 contains spin 3/2 particles. All the particles have the same mass, and the temperature is $T = 0$. Find the ratio of the densities n_1 (gas in compartment 1) and n_2 (gas in compartment 2) if the system is in mechanical equilibrium.

PROBLEM 4 *Score: a+b+c+d=5+5+5+5=20*

The Clausius-Clapeyron equation is:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

a) Describe in words when this equation can be applied and explain all the symbols in the equation.
b) Draw a phase diagram (pressure against temperature) of a substance with three phases (solid, liquid, gas) that expands upon freezing. Indicate the areas in the diagram with a label (solid, liquid or gas) corresponding to the phase of the substance. Also label the phase equilibrium curves (vapour curve, melting curve and sublimation curve). Indicate the triple point and the critical point in the diagram and shortly explain what happens at these points.

Assume that 1) the latent heat L (in Joule per mole) for vaporization is independent of temperature, 2) the vapour obeys the ideal gas law and 3) the volume of the liquid is small compared to the volume of the vapour.

c) Show that under these assumptions the vapour pressure P_{vap} of the substance is given by:

$$P_{vap} = P_{ref}e^{-\frac{L}{RT}}$$

where, P_{ref} is a reference pressure.

d) Calculate the latent heat for vaporization of water from the data in the table below. You may assume that the latent heat is independent of temperature in the range 50-70 °C.
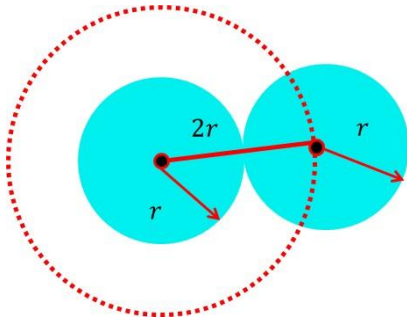
Vapour pressure of water

Temperature (°C)	Pressure (kPa)
50	12.3
70	31.2

Solutions

PROBLEM 1

a)

The total excluded volume for centres of other gas molecules is $\frac{4}{3}\pi(2r)^3$ (see figure above). We have to account for the fact that we need a pair for an excluded volume which gives a factor $\frac{1}{2}$. Furthermore, in the problem it is stated that V is the molar volume, consequently b should also be expressed in molar terms, giving a factor N_a (Avogadro's number). This leads to:

$$b = \frac{1}{2}N_a\frac{4}{3}\pi(2r)^3 = \frac{16}{3}\pi N_a r^3$$

b)
Starting from the ideal gas law (with V the molar volume),

$$PV = RT$$

We first make a correction for the excluded volume which is b: $V \rightarrow V - b$;

We then have

$$P = \frac{RT}{V-b}$$

The real pressure is lower due to the attractive molecular forces pulling the gas molecules away that are close to the walls and exert the pressure. Both the number of molecules that are influenced close to the wall and the 'pulling force' are proportional to the density which itself is proportional to $\frac{1}{V}$. Thus, the pressure reduction is proportional to $\left(\frac{1}{V}\right)^2$. The proportionality constant we denote with a.

In total,

$$P = \frac{RT}{V-b} - a\left(\frac{1}{V}\right)^2 = \frac{RT}{V-b} - \frac{a}{V^2}$$

c)

The derivation of the critical parameters is done in B&B on page 299-300. It is based on solving the following three equations with three unknowns,

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

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

where the lower two equations are the definition of the inflection point.

The last two equations lead to:

$$\frac{-RT}{(V - b)^2} + \frac{2a}{V^3} = 0$$
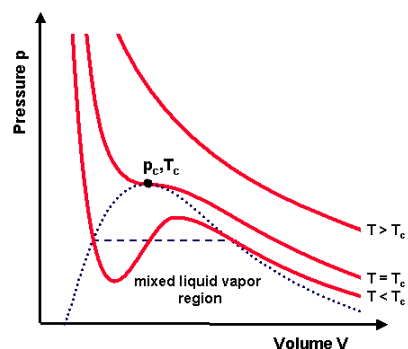
And

$$\frac{2RT}{(V - b)^3} - \frac{6a}{V^4} = 0$$

These two equations only involve T and V and can be rewritten as

$$RT = \frac{2a(V - b)^2}{V^3} = \frac{3a(V - b)^3}{V^4}$$

We then find immediately: $V_c = 3b$ and $T_c = \frac{8a}{27Rb}$

From substituting V_c and T_c in the vdW equation it follows that: $P_c = \frac{a}{27b^2}$

d)

e)

Firstly we have $F = U - TS$ and thus,
$$dF = dU - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$$

From the fact that F is exact:

$$dF = -SdT - PdV = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \Rightarrow$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_V \Rightarrow -\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial^2 F}{\partial V \partial T}\right)_{V,T} = \left(\frac{\partial^2 F}{\partial T \partial V}\right)_{T,V} = -\left(\frac{\partial P}{\partial T}\right)_V \Rightarrow$$

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

From the first law: $dU = TdS - PdV$ we derive,

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

Then we use the Maxwell relation derived above

Substitution directly gives:

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

f)

For a van der Waals gas:

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

Thus,

$$\Delta S = \int_{V_0}^{2V_0} \left(\frac{\partial S}{\partial V}\right)_T dV = \int_{V_0}^{2V_0} \left(\frac{\partial P}{\partial T}\right)_V dV = \int_{V_0}^{2V_0} \frac{R}{V - b} dV = R \ln\left(\frac{2V_0 - b}{V_0 - b}\right)$$

And

$$\Delta U = \int_{V_0}^{2V_0} \left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_0}^{2V_0} \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right) dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\frac{R}{V - b} - \frac{RT}{V - b} + \frac{a}{V^2} = \frac{a}{V^2}$$

$$\Delta U = \int_{V_0}^{2V_0} \frac{a}{V^2} dV = a\left(\frac{1}{V_0} - \frac{1}{2V_0}\right) = \frac{a}{2V_0}$$

The entropy change is positive because a free expansion is an irreversible process. The change in internal energy is also positive. This can be explained in terms of the attractive intermolecular forces. The potential energy U_{pot} due to the attraction of the molecules becomes less negative when these molecules are farther apart (as is the case after the expansion). Thus, the potential energy U_{pot} part of the total internal energy U increases. The kinetic energy part U_{kin} remains constant as the expansion is isothermal. Consequently, the total internal energy $U = U_{pot} + U_{kin}$ increases.

PROBLEM 2

a)
The change in internal energy $U_2 - U_1$ is due to the work done *on* the gas $(p_1 V_1)$ when pushing it through the throttle and the work done *by* the gas $(-p_2 V_2)$ when pushing away the gas at lower pressure.

Thus $U_2 - U_1 = p_1 V_1 - p_2 V_2 \Rightarrow U_2 + p_2 V_2 = U_1 + p_1 V_1 \Rightarrow H_2 = H_1$

Note that the system is isolated so, $dQ = 0$ and only changes in the internal energy due to work are possible.

b)

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H$$

Using that H is an exact differential and starting from the constant enthalpy $(dH = 0)$ we find,

$$dH = 0 = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \Rightarrow \left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}$$

From

$$dH = dU + pdV + Vdp = TdS - pdV + pdV + Vdp = TdS + Vdp$$

And the Maxwell equation that is given, we find,

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

We also have that at constant pressure: $dH = TdS = \bar{d}Q \Rightarrow C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$

So that we can write:

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}$$

c)

We rewrite:

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V}$$

to

$$V = \frac{RT}{p}\left(1 + \frac{B(T)}{V}\right)$$

And we approximate the V in the correction term by $V = \frac{RT}{p}$ (so neglecting the correction term in the correction term itself). This leads to:

$$V \approx \frac{RT}{p}\left(1 + \frac{pB(T)}{RT}\right) = \frac{RT}{p} + B(T)$$

and,

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \frac{\partial B(T)}{\partial T}$$

Using this in the expression derived in b)

$$\mu_{JK} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} = \frac{1}{C_p}\left(T\frac{R}{p} + T\frac{\partial B(T)}{\partial T} - \frac{RT}{p} - B(T)\right) = \frac{1}{C_p}\left(T\frac{\partial B(T)}{\partial T} - B(T)\right)$$

d)
To calculate the Joule-Kelvin coefficient we need the second virial coefficient $B(T)$ of the van der Waals gas.

The virial expansion is defined as:

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \cdots$$

Rewrite the van der Waals equation as:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \Rightarrow$$

$$\frac{PV}{RT} = \frac{1}{\left(1 - \frac{b}{V}\right)} - \frac{a}{RTV}$$

and expand the first term on the right hand side in powers of $\frac{1}{V}$:

$$\frac{PV}{RT} = \left(1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \cdots\right) - \frac{a}{RTV} \Rightarrow$$

$$\frac{PV}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + b^2\frac{1}{V^2} + \cdots$$

Thus,

$$B(T) = b - \frac{a}{RT}$$

Using this in the expression of c) we have:

$$\mu_{JK} = \frac{1}{C_p}\left(T\frac{\partial B(T)}{\partial T} - B(T)\right) = \frac{1}{C_p}\left(T\left(\frac{a}{RT^2}\right) - b + \frac{a}{RT}\right) = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

e)

From the expression derived in d) we conclude that for very low temperatures $\mu_{JK} > 0$ and for very high temperatures $\mu_{JK} < 0$.

As

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{T_2 - T_1}{p_2 - p_1}$$

we see that because $p_2 - p_1 < 0$ in the Joule-Kelvin process we have $T_2 - T_1 > 0$ (heating) if $\mu_{JK} < 0$ and $T_2 - T_1 < 0$ (cooling) if $\mu_{JK} > 0$.

Thus, heating for high temperatures and cooling for low temperatures.

PROBLEM 3

a)

Use the hint to find the density of states as a function of energy. Remember to multiply with a factor of $2S + 1$ because of the spins states of the spin S fermion.
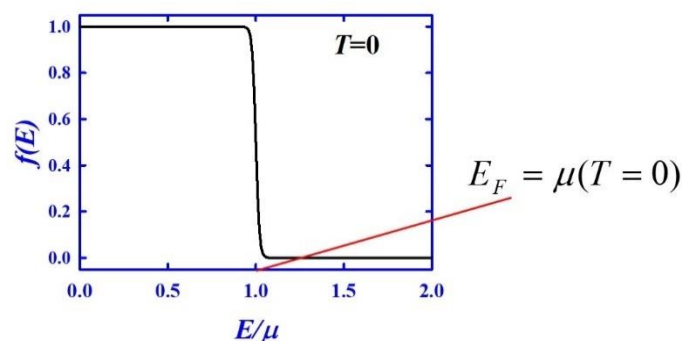
$$g(p)dp = (2S + 1)\frac{V}{h^3} 4\pi p^2 dp \xrightarrow[p=\sqrt{2mE}]{} g(E)dE$$

$$= \frac{V(2S + 1)}{\left(\frac{h}{2\pi}\right)^3}\frac{1}{2\pi^2}\left(\sqrt{2mE}\right)^2 d\left(\sqrt{2mE}\right)$$

$$= \frac{V(2S + 1)}{\hbar^3}\frac{1}{2\pi^2}\left(\sqrt{2mE}\right)^2\frac{\sqrt{2m}}{2\sqrt{E}}dE = \frac{V(2S + 1)}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}dE$$

b)

The definition of the Fermi energy is $E_F = \mu(T = 0)$.

The function $f(E)$, becomes a step function when $T = 0$. When $E < E_F$ the argument of the exponent goes to minus infinity and $f(E) = 1$; when $E > E_F$ the argument of the exponent goes to infinity and $f(E) = 0$.

Sketch should look like:

c)

The number of fermions N is given by:

$$N = \int_0^\infty f(E)g(E)dE \xrightarrow[T\to 0]{} N = \int_0^{E_F} g(E)dE = \frac{V(2S + 1)}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^{E_F}\sqrt{E}dE$$

$$= \frac{V(2S + 1)}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\frac{2}{3}E_F^{\frac{3}{2}} \Rightarrow$$

$$E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S + 1}\frac{N}{V}\right)^{\frac{2}{3}}$$

d)

The energy U is given by:

$$U = \int_0^\infty Ef(E)\,g(E)dE \underset{T\to 0}{\Longrightarrow} U = \int_0^{E_F} Eg(E)dE = \frac{V(2S+1)}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^{E_F} E^{\frac{3}{2}}dE$$

$$= \frac{V(2S+1)}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\frac{2}{5}E_F^{\frac{5}{2}}$$

$$= \frac{V(2S+1)}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\frac{2}{5}\left(\frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S+1}\frac{N}{V}\right)^{\frac{2}{3}}\right)^{\frac{5}{2}} =$$

$$= \frac{(2S+1)}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{\hbar^2}{2m}\right)^{\frac{5}{2}}\frac{12}{20}\left(\frac{6\pi^2}{2S+1}\right)^{\frac{5}{3}}\frac{N^{\frac{5}{3}}}{V^{\frac{2}{3}}} = \frac{3}{5}\frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S+1}\right)^{\frac{2}{3}}\frac{N^{\frac{5}{3}}}{V^{\frac{2}{3}}}$$

e)
For mechanical equilibrium the pressure in both compartments should be equal.

The pressure for the gases follows from:
$$dU = TdS - PdV + \mu dN \underset{T\to 0}{\Longrightarrow} P = -\left(\frac{dU}{dV}\right)_N$$

$$P = -\frac{d}{dV}\left(\frac{3}{5}\frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S+1}\right)^{\frac{2}{3}}\frac{N^{\frac{5}{3}}}{V^{\frac{2}{3}}}\right) = -\left(\frac{3}{5}\frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S+1}\right)^{\frac{2}{3}}\left(-\frac{2}{3}\right)\frac{N^{\frac{5}{3}}}{V^{\frac{5}{3}}}\right)$$

$$= \frac{2}{5}\frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S+1}\right)^{\frac{2}{3}}n^{\frac{5}{3}}$$

with $n = \frac{N}{V}$ the density of the gas.
For mechanical equilibrium we should have:

$$P_1 = P_2 \Rightarrow \left(\frac{n_1}{n_2}\right)^{\frac{5}{3}} = \left(\frac{2\times\frac{1}{2}+1}{2\times\frac{3}{2}+1}\right)^{\frac{2}{3}} = \left(\frac{2}{4}\right)^{\frac{2}{3}} \Rightarrow \frac{n_1}{n_2} = \left(\frac{1}{2}\right)^{\frac{2}{5}}$$

PROBLEM 4

a)

This equation can be applied in the situation of a phase transition between, say, phase 1 and phase 2 of a one-component system. ΔS and ΔV are the change in entropy and volume when a certain amount (1 molecule, 1 gram, 1 mole etc.) of the substance is transformed from phase 1 to phase 2. The equation then relates these changes to the slope of the equilibrium curve in the PT-diagram.

b)

The diagram is given in the sketch.
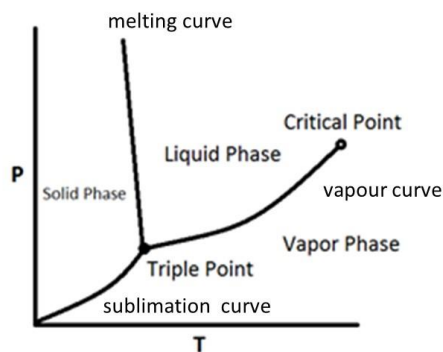
The slope of the melting curve should be negative because it was given that the compound expands upon freezing. The Clausius-Clapeyron equation gives the slope of the melting curve. In the transformation from solid to liquid the entropy increases ($\Delta S = S_{liquid} - S_{solid} > 0$). We have a negative slope because $\Delta V = V_{liquid} - V_{solid} < 0$, because the volume of the substance decreases upon melting (expands upon freezing).

Critical point: If we proceed along the vapour curve to higher temperatures the latent heat of vaporization decreases and becomes zero at the critical point, also the volume change of the phase transition becomes zero at this point. At temperatures and pressure higher than the temperature and pressure of the critical point there is no difference between the liquid and the gas phase.

Triple point: All three phases coexist.

c)

The entropy change per mole is $\Delta S = \frac{L}{T}$.

The volume change is $\Delta V = V_{vap} - V_{liquid} \approx V_{vap}$

The ideal gas law for one mole of vapour is : $P_{vap} V_{vap} = RT$.

Then from the Clausius-Clapeyron equation we find,

$$\frac{dP_{vap}}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T} \frac{1}{V_{vap}} = \frac{L P_{vap}}{RT^2} \Rightarrow$$

$$\frac{dP_{vap}}{P_{vap}} = \frac{LdT}{RT^2} \Rightarrow d\ln P_{vap} = d\frac{-L}{RT} \Rightarrow \ln P_{vap} = \frac{-L}{RT} + const. \Rightarrow P_{vap} = P_{ref}e^{-\frac{L}{RT}}$$

d)

$$T_1 = 50°C = 323.15 \text{ K}; \ T_2 = 70°C = 343.15 \text{ K}$$
$$P_1 = 12.3 \text{ kPa}; \ P_2 = 31.2 \text{ kPa}$$

Using c)

$$\frac{P_1}{P_2} = e^{-\frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \Rightarrow L = -\frac{R\ln\left(\frac{P_1}{P_2}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \Rightarrow$$

$$L = -\frac{8.314 \times \ln\left(\frac{12.3}{31.2}\right)}{\left(\frac{1}{323.15} - \frac{1}{343.15}\right)} \approx 45 \text{ kJ per mole}$$

This exam was drafted by E.R. van der Graaf and verified by T.A. Schlathölter.

Date: 9-01-2019   Date: 9-01-2019

E.R. van der Graaf   T.A. Schlathölter