HW #2 Solutions

2.1

2.1 What is the boiling point of water on Mt. Evans, Colorado, where the atmospheric pressure is two-thirds that at sea level?

For a liquid $\rightarrow$ gas phase transition we can start with the Clausius - Clapeyron equation:

$$\frac{dP}{dT} = \frac{\ell}{T\Delta v}$$

ℓ: specific latent heat of vaporization
P: pressure
T: temp
Δv: difference in the specific volumes of the gas & liquid

We are trying to get a rough estimate of the change in boiling point so we will need to make some simplifying assumptions. I'm going to assume that ℓ is about constant as a function of temperature and that the specific volume of vapor is so much larger than the specific volume of water that $\Delta v \cong v_{vapor}$. I will also approximate the water vapor as an ideal gas

$$\Rightarrow \Delta v = \frac{V_{ideal}}{m_{vapor}} = \frac{\cancel{n}RT/P}{\cancel{n}\mu_{H_2O}}$$

μ_{H_2O}: molar mass of water

So that the CC equation can be rewritten as

$$\frac{dP}{P} = \frac{dT}{T^2}\frac{\ell\mu_{H_2O}}{R}$$

Integrating from conditions at sea level to conditions at the top of Mt. Evans

$$\Rightarrow \ln\frac{P}{P_0} = \frac{\ell\mu_{H_2O}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

T, P: boiling temp & standard pressure @ Mt. Evans

T_0, P_0: boiling temp & standard pressure @ sea level

Solving for T

$$\Rightarrow \frac{\ell\mu_{H_2O}}{R} = T\left(\frac{\ell\mu_{H_2O}}{RT_0} - \ln\frac{P}{P_0}\right)$$

$$\Rightarrow T = \left(\frac{\ell\mu_{H_2O}}{R}\right)\left(\frac{\ell\mu_{H_2O}}{RT_0} - \ln\frac{P}{P_0}\right)^{-1}$$

We can look up all of the quantities on the LHS, while also knowing that $P/P_0 = 2/3$ as stated by the problem.

$\ell = 2265$ kJ/kg $= 2.265$ kJ/g
$R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}
$\mu_{H_2O} \cong 18$ g/mol
$T_0 = 373$ K $\cong 100°C$

$$\boxed{T \cong 362 \text{ K} = 88°C}$$

This is actually close to the real-life value: ~85C @ 14,500 ft.

Rule of thumb is that you lose about 0.5°C per 500 ft.

2.3

2.3 A cloud chamber contains water vapor at its equilibrium vapor pressure $P_\infty(T_0)$ corresponding to an absolute temperature T_0. Assume that

    (i) the water vapor may be treated as an ideal gas;

    (ii) the specific volume of water may be neglected compared to that of the vapor;

    (iii) the latent heat l of condensation and $\gamma = c_P/c_V$ may be taken to be constants: $l = 540$ cal/g, $\gamma = \frac{1}{2}$.

(*a*) Calculate the equilibrium vapor pressure $P_\infty(T)$ as a function of the absolute temperature T.

(*b*) The water vapor is expanded adiabatically until the temperature is T, $T < T_0$. Assume the vapor is now supersaturated. If a small number of droplets of water is formed (catalyzed, e.g., by the presence of ions produced by the passage of an α particle), what is the equilibrium radius of these droplets?

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(*c*) In the approximations considered, does adiabatic expansion always lead to supersaturation?

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a) This problem asks me to make the same set of assumptions as problem (2.1); therefore I'll just start with the integrated form

$$\ln P/P_0 = \frac{l\mu}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$P = \alpha e^{-l\mu/RT} \qquad \text{when } \alpha \equiv P_0 e^{l\mu/RT_0}$$

The difference this time is that our limits of integration have changed and therefore $P, P_0, T,$ & T_0 refer to different quantities in this problem. P_0 & T_0 are just some arbitrary initial temperature & pressure configuration, which essentially form a constant of integration, which I define as α. For this problem P corresponds w/ $P_\infty(T)$, which we are solving for.

$$\Rightarrow \boxed{P_\infty(T) = \alpha e^{-l\mu/RT}}$$

b) A water droplet will only remain in equilibrium with the water vapor when

$$P_{vapor} = P_r(T) = P_\alpha(T)e^{\frac{2\sigma m/\rho(1/kTr)}{}} \qquad \text{(Huang Eqn. 2.25)}$$

σ: surface tension coefficient r: radius of droplet

m: mass of gas molecule ρ: density of gas

So I will rewrite this in terms of the constants I've already been using and define $a \equiv 2\sigma\mu/\rho R$ & $b \equiv l\mu/R$

$$\Rightarrow P_{vapor} = \alpha e^{(a/r - b)/T}$$

Solving for r we find

$$T \ln{}^{P_{vapor}}\!/_\alpha = \frac{a}{r} - b$$

$$\Rightarrow r = a\left(T \ln{}^{P_{vapor}}\!/_\alpha + b\right)^{-1}$$

We know that the vapor was adiabatically expanded to a temperature T ∴ we just need to determine P_{vapor}. We can determine this by taking advantage of

$$PV^\gamma = \text{const} \quad \text{for adiabatic expansions}$$

and using $\quad V = \frac{NkT}{P}$

$$\Rightarrow P^{1-\gamma} T^\gamma = \text{const}$$

$$\Rightarrow PT^{-\gamma/(\gamma-1)} = \text{const}$$

So we find that $\quad P_\infty(T_0) T_0^{-\gamma/(\gamma-1)} = P_{vapor} T^{-\gamma/(\gamma-1)}$

Since the gas initially has a temperature T_0 and normal (saturated) vapor pressure $P_\infty(T_0)$.

$$\Rightarrow P_{vapor} = P_\infty(T_0)\left(\frac{T}{T_0}\right)^{\gamma/\gamma-1} = \alpha e^{-b/T_0}\left(\frac{T}{T_0}\right)^{\gamma/\gamma-1}$$

Or solving for the radius

$$r = a\left[T \ln\left[e^{-b/T_0}\left(\frac{T}{T_0}\right)^{\gamma/\gamma-1}\right] + b\right]^{-1}$$

$$= a\left[-\frac{T}{T_0}b + b + \frac{T}{\gamma-1}\ln\left(\frac{T}{T_0}\right)T\right]^{-1}$$

$$\boxed{r = a\left[b\left(1-\frac{T}{T_0}\right) + T\frac{\gamma}{\gamma-1}\ln\left(\frac{T}{T_0}\right)\right]^{-1}}$$

w/ $\frac{b}{a} = \rho\ell/2\sigma$

$\frac{1}{a} = \frac{\rho R}{2\sigma\mu} = \frac{\rho k}{2\sigma m}$

c) So this might be a good time to stop and think, what is actually going on here and what does Huang mean by supersaturation?
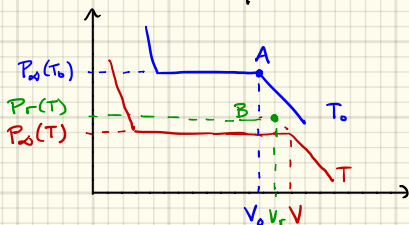
Supersaturation for a vapor is a state in which the partial pressure of the vapor is greater than its equilibrium vapor pressure. It's a state of unstable equilibrium — meaning that a small perturbation to the system will lead to an increased rate of condensation until the system reaches a stable equilibrium (when the pressure falls to the equilibrium vapor pressure).

So what does Huang mean by supersaturation? Well Huang pictures it as a state in (P, V) space that does not lie on the path of an isothermal expansion at temperature T.

If you look @ Huang's solution to problem 2.3(c), you'll notice that he tries to use this understanding of supersaturation to "prove" that <u>yes</u> supersaturation is guaranteed as a result of adiabatic expansion under the problem's assumptions.

His argument is fairly indecipherable, because he uses terms he doesn't really define, but it goes something like this:

An adiabatic expansion will lead to the gas cooling to a temperature T. Therefore let's consider the isothermal paths for constant T & T_0 in (P,V) Space:

The system starts @ point A with T_0, V_0 & $P_{\infty}(T_0)$ defining the system.

Then Huang states that we can clearly see that $V > V_r$ b/c of our assumption of the form of $P_r(T)$, $P_{\infty}(T)$, & using the ideal gas law.

But he never proves that the state <u>has</u> to pass through point B under the adiabatic transformation. In short, my interpretation of Huang's solution is yes, because it does. Maybe someone else has deciphered it.

Here is my alternative approach:

Supersaturation requires that the new pressure after an adiabatic expansion is greater than $P_{\infty}(T)$, assuming the expansion leads to the system cooling to a temp T

$$\Rightarrow \frac{P_{ad}(T)}{P_{\infty}(T)} > 1 \quad \text{where} \quad P_{ad} = P_{\infty}(T_0)\left(\frac{T}{T_0}\right)^{\gamma/\gamma-1}$$

due to adiabatic expansion

From our assumptions, we determined $P_{\infty}(T') \sim e^{-b/T'}$ w/ $b = \ell\mu/R$

$$\Rightarrow \frac{P_{ad}}{P_{\infty}} = \frac{e^{-b/T_0}}{e^{-b/T}}\left(\frac{T}{T_0}\right)^{\gamma/\gamma-1} = e^{b/T_0\left(T_0/T - 1\right)}\left(\frac{T}{T_0}\right)^{\gamma/\gamma-1} > 1$$

Unfortunately this does not quite give us the answer since the exponential term is greater than 1, but the power term is not. So let's rearrange & take the log

$$\Rightarrow e^{b/T_0(T_0/T - 1)} > \left(\frac{T_0}{T}\right)^{\gamma/\gamma-1}$$

$$\frac{b}{T_0}\left(\frac{T_0}{T} - 1\right) > \frac{\gamma}{\gamma-1}\ln\left(\frac{T_0}{T}\right)$$

Define the quantity $x \equiv \frac{T_0-T}{T_0} \Rightarrow T/T_0 = 1-x$

$$\Rightarrow \frac{b}{T_0}\left(\frac{1}{1-x} - 1\right) > \frac{-\gamma}{\gamma-1}\ln(1-x)$$

Both can be expanded in powers of x since $x < 1$ & the radius of convergence is $|x| < 1$ for both series. Then we can compare on order by order basis!

$$\Rightarrow \frac{b}{T_0}\left(x + x^2 + x^3 + x^4 + \cdots\right) > \frac{r}{r-1}\left(x + \frac{x^2}{2} + \frac{x^3}{3} + \frac{x^4}{4} + \cdots\right)$$

Therefore adiabatic expansion will definitely lead to supersaturation if the following condition is satisfied:

$$\boxed{\frac{b}{T_0} > \frac{r}{r-1}}$$

Recall that $r = \frac{3}{2}$ and $b = \ell\mu/R \simeq 4900 \text{ K}$ for water vapor. Since the critical point of water is below 700 K, then it is safe to say that this is satisfied by any reasonable water vapor system.

Therefore, <u>yes</u>, under our assumptions, Adiabatic expansion always leads to Supersaturation.

2.4

2.4 Show that the heat capacity at constant volume C_V of a Van der Waals gas is a function of the temperature alone.

We know that C_V is given by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Therefore we need to obtain a form for the internal energy of the Van der Waals gas as a function of temperature T & volume V. A Van der Waals gas follows the equation of state

$$P = \frac{nRT}{V-b} - \frac{a}{V^2} \qquad (1)$$

From the first law of thermodynamics we know that

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

however it is not clear how to hold S constant in Eqn (1). Therefore we can recall the more accessible relation between pressure & the Helmholtz potential $A = U - TS$

$$\Rightarrow dA = -SdT - PdV \quad \text{or} \quad P = -\left(\frac{\partial A}{\partial V}\right)_T, \quad S = -\left(\frac{\partial A}{\partial T}\right)_V$$

Integrating at a constant temperature from initial volume V_0 to find volume V

$$\Rightarrow A = -nRT \ln\left(\frac{V-b}{V_0-b}\right) - \frac{aV_0}{V} + C(T)$$

where $C(T)$ is an integration constant that can depend on T, since T was taken to be a constant during integration. The exact expression for $C(T)$ is not important, since we only need to demonstrate that C_V only depends on T, not <u>how</u> it depends on T.

Since $U = A + TS$, we must also determine the form of S

$$\Rightarrow S = -\left(\frac{\partial A}{\partial T}\right)_V = nR \ln\left(\frac{V-b}{V_0-b}\right) - C'(T)$$

where a $(')$ denotes differentiation with respect to temperature

$$\Rightarrow U = C(T) - \frac{aV_0}{V} - TC'(T)$$

Now we can finally solve for C_V

$$\Rightarrow \boxed{C_V = -T\, C''(T)}$$

which clearly depends on T & not V.