1. (30 points) Short answer questions. 3 points each. Complete sentences are unnecessary.

a) Give two real world examples of processes that use multiple phases to separate mixtures of components.

Correct answers include: distillation; liquid extraction; crystallization; gas absorption.
- Need to have two actually different processes, and show that you know phases are involved (e.g. “separation of benzene and toluene” is not enough; need “by distillation”)

b) Identify one way to find the vapor pressure of a compound at a given temperature.

Correct answers include: Antoine equation; Clausius-Clapeyron equation; tabulated data; P-T phase diagram

c) Write the Gibbs phase rule, define each variable in the equation, and give an example of a system in which there is one degree of freedom.

DF (degrees of freedom) = 2 + C (# components) - π (# phases)
System should have one component, two phases (or two components, three phases), e.g. water at vapor-liquid equilibrium

d) Air and water are present in a two-phase system in which the liquid phase is entirely composed of water. Write an expression for the mole fraction of air at the interface in terms of the water vapor pressure p*(T) and the total pressure P. What assumptions did you make?

Raoult: $y_{water}P = x_{water}P^*_{water}(T)$ and $x_{water} = 1$, so $y_{water} = P^*_{wate}(T)_r/P$
$y_{air} = 1 - y_{water} = 1 - P^*_{water}(T)/P$
Assuming: Ideal gas, ideal liquid, at equilibrium

e) For a gas with 1 mole percent ethane vapor in contact with liquid water at 20 °C and 10 atm, what is the mole fraction of ethane in the liquid phase if the mixture obeys Henry's law such that $H_{ethane} = 1 \times 10^4$ atm?

Henry's law: $y_i P = x_i H_i$
$x_i = (0.01)(10 \text{ atm}) / (1 \times 10^4 \text{ atm}) = 10^{-5}$

f) Write the energy balance equations for (i) an open system at steady-state and (ii) a closed system, defining all terms. State your assumptions including the sign conventions for heat and work.

Closed system: $\Delta E_k + \Delta E_p + \Delta U = Q - W_s$
Open system: $\Delta E_k + \Delta E_p + \Delta H = Q - W_s$

Where ΔE_k is kinetic energy; ΔE_p is potential energy; ΔU is internal energy; ΔH is enthalpy; Q is heat entering the system; W_s is shaft work done by the system

g) Consider a constant-volume, closed, adiabatic system with no shaft work and no change in kinetic or potential energy. From the energy balance, ΔU must be zero. However, if an exothermic chemical reaction occurs, the temperature in the system rises. How is this possible?

Internal energy depends on both temperature and chemical composition; system temperature rises, but internal energy associated with composition (bond energy) goes down, so there is no net effect on the internal energy.

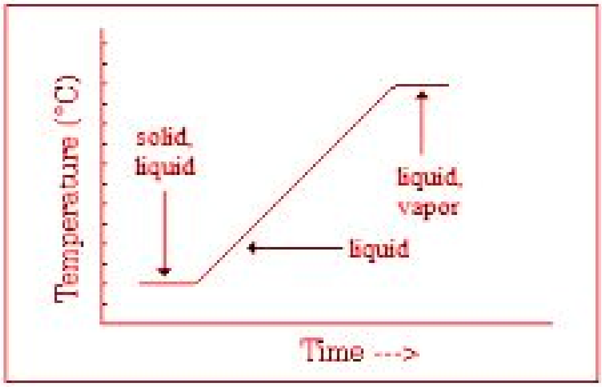
h) What are the defining equations for heat capacity at constant volume and heat capacity at constant pressure?

$C_V = dU/dT$ at constant V or $\Delta U = \int C_V \, dT$
$C_P = dH/dT$ at constant P or $\Delta H = \int C_P \, dT$

i) What does it mean to say that internal energy is a 'state variable'?

Changes in state variables like internal energy are path-independent.

j) Sketch an approximate temperature vs. time plot for a constant pressure, closed system in which a pure substance initially in solid phase at its melting point is heated at a constant rate to a vapor at its boiling point. Label the phase(s) present in each region.

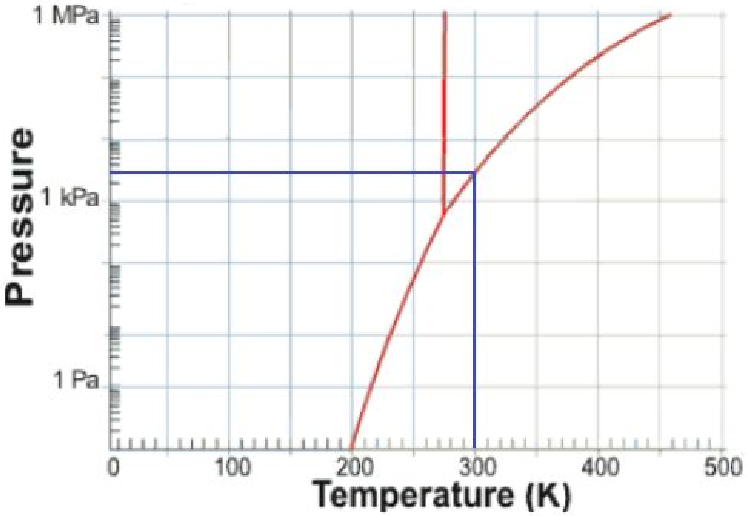


Sketch should include:

- Flat region as solid melts (solid, liquid phases present)
- A ~linear rise in temperature as liquid is heated (only liquid phase present).
- Flat again as liquid vaporizes (liquid, vapor phases present).

2. A fishy tank (30 points)

1 kPa = 0.01 atm = 7.6 mmHg



a) Both of your roommates are allergic to cats, so in your search for affection you decide to build an aquarium instead. You set the temperature of the 40 L tank at 27 °C and fill it with 10 L of dry air at 1 atm and 30 L of liquid water. After you close the lid, 0.2 g of the water evaporates into the air so that the tank is at equilibrium. What is the total pressure inside the tank? *Hint: At 0 °C and 1 atm, 1 mol of an ideal gas fills 22.4 L.* (15 points)

From the graph, p*(300) = 3 kPa = 0.03 atm.

Method 1:
Initial number of moles of gas = (10 L ideal gas) / (22.4 L/mol) * (273/300) = 0.40625 mol
Number of moles of water evaporating = 0.2 g / (18 g/mol) = 0.0111 mol
Method 1a : Total number of moles of gas = initial number of moles of gas + number of moles evaporated = 0.0111 + 0.40625, so y_{H2O} = 0.0111 / (0.0111 + 0.40625) = 0.02662
Method 1b: After evaporation: Same volume of gas, still an ideal gas, PV = nRT so total moles gas is 0.40625, so: y_{H2O} = 0.0111 / 0.40625 = 0.02735 (less correct, because how can the moles of air have decreased?)
Either way, then: Raoult's Law: y_i * P = p* → P = p* / yi = 0.03 atm / 0.02662 = **1.1 - 1.2 atm**

Alternatively, Method 2:

P_{air} is 1 atm (it was 1 atm at the start, and its V, n, and T are not changing). $P_{water} = y_{water}P = P^*_{water}$, which we can read off of the graph (0.03 atm). $P_{total} = P_{air} + P_{water}$ = 1.03 atm.

b) After a few days your new friends look a bit chilly, so you change the temperature in the tank to 30 °C. You flip open the chemical engineering handbook of your choice to look up the constants associated with the Antoine equation for water, but you accidentally spill some water on the page, smudging the value of A. You can still read that B and C are 1750.286 and 235.000, respectively. Use the conditions given in part a) to calculate the constant A and determine the vapor pressure of water in the tank at the new temperature using Antoine's equation. (15 points)

Antoine's equation: $\log_{10} p^*(T) = A - B / (T + C)$
0.03 atm = 22.8 mmHg
$\text{Log}_{10}(22.8 \text{ mmHg}) = A - 1750.286 / (27 + 235)$
$A = 8.038$
$\text{Log}_{10}\ p^*(30\text{ C}) = 8.038 - 1750.286 / (30 + 235)$
$p^*(30\text{ C}) = 27.1373$ mmHg = **0.0357 atm**

3. A cup of tea (40 points)

a) You wake up feeling a bit under the weather, so you decide to make a cup of tea. You pour 500 g of tap water at 25 °C into your electric kettle and turn it on. The kettle operates at 1300 W and takes two minutes to heat your water to its boiling point. What is the heat capacity of the water over this temperature range in J/(g °C)? (8 points)

Need 1 W = 1 J/s
1300 J/s * 120 s = Cp * 500 g * (100 - 25 C)
Cp = **4.16 J/g C**

b) You put your tea in your reusable thermos and leave for class. You know that in order to avoid burning yourself, you need to wait until the tea is at 60 °C before drinking it. Using the heat capacity you calculated in part a), how much energy in kJ needs to be removed from the tea to cool it to 60 °C? (8 points)

From the energy balance, Q = ΔH (no work, no change in PE, KE)
Q = m Cp (T_f-T_i) = 500 g * 4.16 J/g C * 40 C = **83.2 kJ**

c) The tea cools down over time as described by Newton's law of cooling, which states that

$$T(t) = T_{out} + (T_{init} - T_{out})e^{\frac{-hAt}{mC_p}}$$

where T_{out} = the temperature outside the thermos, T_{init} = the initial temperature of the tea, h = the heat transfer coefficient of the thermos, A = the total surface area of the thermos, m = the mass of tea in the thermos, and C_p = the heat capacity of the tea. Your thermos is cylindrical with a radius of 3.5 cm and a height of 13 cm. Given h = 1.2 W/(m^2 K), how many hours should you wait before you drink your tea? (12 points)

A cylinder has a rectangle and two circles:
A = 2 * pi*(3.5 cm)^2 + 13 cm*2*pi*3.5 cm = 362.9 cm^2
T(t) = 25 + 75 exp (-1.2 W/m^2 C * 362.9 cm^2 / (4.16 J/g C * 500 g) * t)
For a final temperature of 60 C: 35/75 = exp(-2.09*10^{-5} * t)
Therefore t = 36,392 seconds = **10 hours**

d) You are feeling impatient, so you remove the top of your thermos, allowing water to evaporate. Given that the latent heat of vaporization of water is 2257 J/g, how much water would have to evaporate to cool the remaining water to 60 °C? You may neglect heat loss through the walls of the thermos.*Hint: Not all of the water will be cooled, so your answer from part b) no longer applies.* (12 points)

Some amount, m_{vap}, will vaporize, absorbing heat from the liquid that does not vaporize; the amount of heat that it takes to vaporize will be the amount that is taken from the remaining liquid, cooling the liquid by 40 C.

m_{liq} * (4.18 J/g C) * (40 C) = (2257 J/g) * m_{vap}
Given that there are 500 g total, m_{liq} = 500 - m_{vap}
Isolate m_{vap}: (500 g) * (4.16 J/g C) * (40 C) = m_{vap} [(4.16 J/g C) * (40 C) + 2257 J/g]
Solve to get m_{vap} = **34.5 g**