\[ R = 8.3 \ J/(K \cdot \text{mol}) = 0.082 \ \text{L} \cdot \text{atm}/(K \cdot \text{mol}) \]

1 bar = 10^5 Pa

\[ \Delta U = q_y - P_{\text{ext}} \Delta V \]

\[ dU(S,V,\{n_i\}) = TdS - PdV + \sum_i \mu_i dn_i \]

\[ dH(S,P,\{n_i\}) = TdS + VdP + \sum_i \mu_i dn_i \]

\[ dA(T,V,\{n_i\}) = -SdT - PdV + \sum_i \mu_i dn_i \]

\[ dG(T,P,\{n_i\}) = -SdT + VdP + \sum_i \mu_i dn_i \]

\[ nd\mu(T,V) = -SdT + VdP \]

\[ H = U + PV \]

\[ A = U - TS \]

\[ G = H - TS = \sum_i \mu_i n_i \]

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad ; \quad C_P = \left( \frac{\partial H}{\partial T} \right)_P \]

\[ \left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P \quad ; \quad \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \]

\[ \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

\[ \alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]

\[ P_1 V_1^\gamma = P_2 V_2^\gamma \quad ; \quad \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma - 1} \quad = \left( \frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} \]

\[ \gamma = C_P/C_V \quad ; \quad \text{adiabatic process} \]

\[ \Delta G^o = -RT \ln K(T) \]

\[ H = -T^2 \left( \frac{\partial (G/T)}{\partial T} \right)_P \quad ; \quad U = -T^2 \left( \frac{\partial (A/T)}{\partial T} \right)_V \]

\[ F = 2 + C - P \]
1. The laws

(a) (16 pts) State the First and Second Laws of Thermodynamics in terms of properties of the universe and next, in terms of properties of the system. Define the terms in the equations.

Universe

\[ \Delta E = 0 \quad \text{energy is conserved} \]
\[ \Delta S > 0 \quad \text{entropy is constantly increasing} \]

System

\[ \Delta E = dq_{by} + dq_{won} \quad \text{the change in energy of a system is given by} \]
\[ \text{the heat absorbed and the work done on the system} \]
\[ T \Delta S \geq dq \quad \text{the change in entropy always exceeds the heat absorbed} \]

(b) (8 pts) Prove that the Gibbs energy of the system decreases for all spontaneous processes that occur when the temperature is constant and the system and external pressure are equal and constant.

\[ Tds \geq dq, \quad dg = dU + P_{ext} dv \]
\[ H = U + PV, \quad dH = dU + Pdv + Vdp \]

\[ Tds \geq dH - Pdv - Vdp + P_{ext} dv \]

If \( P = P_{ext} = \text{const} \)
\[ Tds \geq dH \]

If \( T = \text{constant} \)
\[ 0 \geq dH - Tds = d(H - TS) = dG \]
\[ \Delta \quad 0 \geq dG \]
2. (32 pts) Complete Table I for the processes in which one mole of water vapor, initially at the state point $P_I, V_I, T_I$ is expanded to a final volume of $10V_I$ via the following paths. Assume water is an ideal gas with $C_v = 3R$. Express your answers in terms of the properties of the initial state.

(a) Constant pressure expansion where $P_{ext} = \frac{1}{2} P_I = P_2$

(b) A reversible expansion at constant $E$.

\[ a) \quad P_1 V_1 = P_2 V_2 \quad \text{ideal gas, } P_2 = \frac{1}{2} P_1, \quad V_2 = 10V_1 \]

\[ T_2 = \frac{P_2}{P_1} \frac{V_2}{V_1} = \frac{1}{2} \cdot 10 = 5 \]

\[ W_{by} = -P_{ext} \Delta V = \frac{1}{2} P_1 (10 - 1) V_1 = \frac{9}{2} P_1 V_1 \]

\[ \Delta E = C_v \Delta T = 3R(4T_I) = 12RT_I \]

\[ b) \quad \text{reversible constant } E \Rightarrow \Delta T = 0, \quad T_2 = T_1 \]

\[ P_1 V_1 = P_2 V_2 \Rightarrow P_1 V_1 = 10V_1 P_2, \quad P_2 = \frac{1}{10} P_1 \]

\[ W_{by} = -\int P \ dl = -RT \ln \left( \frac{V_2}{V_1} \right) = -RT \ln (10) \]
3. (16 pts) Provide numerical values in Table II appropriate to one mole of liquid water at 300K given that $C_P = 9R$, $\kappa T = 5 \times 10^{-5} \text{ bar}$, $\alpha_P = 6 \times 10^{-4} \text{ K}^{-1}$, $K_f = 2 \text{ K/(mol/kg)}$.

(a) Calculate the fractional change in volume when the temperature is increased by 10 K at a fixed pressure of 1 bar;

(b) if the temperature changes by 10 K, what is the change in H at a pressure of 1 bar?

(c) when the volume is decreased by ten percent at constant T and at one bar pressure, what is $\Delta P^A$?

(d) what is the change in freezing point when 2 moles of dimerizing solute are added to a kilogram of water.

\[
\begin{align*}
\text{TABLE II: The times are changing.} \\
| a, \Delta V/V | 6 \times 10^{-3} \\
| b, \Delta H | 90 \text{R} \cdot \text{K} \\
| c, \Delta P^A | -0.1 \text{ bar} \\
| d, \Delta T | 2 \text{ K} \\
\end{align*}
\]

\[
\begin{align*}
\text{(a)} & \quad \alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \Rightarrow \quad \frac{\Delta V}{V} = \alpha_P \Delta T = 6 \times 10^{-4} \cdot 10 \text{ K} = 6 \times 10^{-3} \\
\text{(b)} & \quad \Delta H = C_P \Delta T = 9 \cdot R \cdot 10 \text{ K} \\
\text{(c)} & \quad dA = -\kappa dT - P dV, \quad \frac{\Delta A}{V} = -P \frac{\Delta V}{V} = -1 \text{ bar} \times 0.1 \\
\text{(d)} & \quad \Delta T = K_f m = \frac{2 \text{ K}}{\text{mol/kg}} \frac{1 \text{ mol}}{\text{kg}} = 2 \text{ K}
\end{align*}
\]
4. (30 pts) Prove the following. Hints: Eq(1), start from \( dG \); Eq(2) start from Eq(1); Eq(3), you are on your own.

\[ nd\mu = -SdT + VdP \]  
(1)

\[ \rho \left( \frac{\partial \mu}{\partial \rho} \right)_T = \left( \frac{\partial P}{\partial \rho} \right)_T \]  
(2)

\[ \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \]  
(3)

(1) \[ dG = d(\mu \cdot n) = nd\mu + \mu d\rho = -SdT + VdP + \mu d\rho \]
\[ nd\mu = -SdT + VdP \]

(2) from the above, divide by \( \partial \rho \) at const \( T \)
\[ n \left( \frac{\partial \mu}{\partial \rho} \right)_T = V \left( \frac{\partial P}{\partial \rho} \right)_T \Rightarrow \rho \left( \frac{\partial \mu}{\partial \rho} \right)_T = \left( \frac{\partial P}{\partial \rho} \right)_T \]

(3) \[ dE = Tds - PdV, \quad \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \]
but \[ dA = -SdT - PdV \Rightarrow \text{Maxwell relation} \]
\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \]
\[ \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \]
5. (12 pts) Binary mixtures.

(a) Sketch the chemical potential vs. temperature for a pure substance with liquid, solid and gas phases.

(b) Next, what is the chemical potential of component 1 in a binary liquid mixture?

(c) Show graphically why the increase in boiling point is always much less than the decrease in freezing point.

\[
d\mu = -\frac{S}{n}dT + \frac{V}{n}dP
\]
7. (8 pts) The mole fractions of oxygen and nitrogen in air at sea level (pressure of 1 bar) are roughly 0.21 and 0.78, respectively. Calculate the mole fractions of these species when dissolved in water. The Henry's law constants for oxygen and nitrogen are, \( k_{\text{oxygen}} = 4.2 \times 10^7 \text{ Pa} \), \( k_{\text{nitrogen}} = 7.8 \times 10^7 \text{ Pa} \). Recall Henry's and Dalton's law.

\[
X_1 \cdot k = Y_1 \cdot P \quad \text{for } O_2 \quad Y_1 \cdot P = 0.21 \text{ bar} = \frac{4.2 \times 10^7 \text{ Pa} \times 1 \text{ bar}}{10^5 \text{ Pa}}
\]

\[
X_1 = \frac{0.21}{4.2 \times 10^2} = 5 \times 10^{-4}
\]

for \( N_2 \),

\[
Y_2 \cdot P = 0.78 \text{ bar} = \frac{7.8 \times 10^7 \text{ Pa} \times 1 \text{ bar}}{10^5 \text{ Pa}}
\]

\[
X_2 = \frac{0.78}{7.8 \times 10^2} = 10 \times 10^{-4} = 1 \times 10^{-3}
\]

8. (12 pts) First and second order transitions.

(a) Plot the temperature dependence of a quantity (label the quantity) as it passes through a first order transition.

(b) If a liquid and a gas phase of a pure substance coexist in equilibrium, what are two conditions that must be satisfied?

(c) When a transition is labelled as second order, what criterion is satisfied?

\[\begin{align*}
P_{\text{gas}} &= P_{\text{eq}} \quad \text{and of course in general } \\
T_{\text{gas}} &= T_{\text{eq}}
\end{align*}\]

\[\begin{align*}
\left(\frac{\partial^2 G}{\partial T^2}\right)_P \quad \text{or } \\
\left(\frac{\partial^2 G}{\partial P^2}\right)_T
\end{align*}\] has an infinity at the transition.
6. (16 pts) Osmotic pressure.

(a) Define the osmotic pressure.

(b) Recall that for an ideal liquid solution the osmotic pressure of the solvent II obeys

\[
\Pi = \frac{n_2 RT}{V} = c_2 RT
\]

where \( n_2 \) is the number of moles of dissolved substance and \( c_2 \) the molar concentration. Write a virial expansion for \( \Pi \) following the conventions and notations used for non-ideal gases.

(c) The osmotic pressure of polymer solutions shows a critical point. In direct analogy with gas-liquid behavior, what are the two conditions (equations) for a critical point?

(d) What happens to the liquid solution for temperatures less than the critical temperature?

a) The pressure one must exert on a binary fluid so that it is not further diluted by solvent, when the fluid and its pure solvent are separated by a membrane permeable to solvent alone.

b) \( \Pi = C_2 RT \left\{ 1 + B_2 c_2 + B_3 c_2^2 + \ldots \right\} \), \( C_2 \) osmotic virial coefs.

c) \( \left( \frac{\partial^2 \Pi}{\partial c_2^2} \right)_T = \left( \frac{\partial^3 \Pi}{\partial c_2^3} \right)_T = 0 \)

d) Polymer solution separates into two phases, one rich in polymer + the other dilute.
9. (24 pts) The phase diagram below represents gas, liquid and solid phases. The following points have special names attributed to them. Provide these terms:

(a) boiling pt of pure A
(b) azeotrope mixture
(c) eutectic pt
(d) melting pt of pure A

Identify the phases present
(e) gas + liquid
(f) two liquid phases with differing mole fractions of A,B
(g) liquid A+B
(h) solid A, liquid A+B
10. (12 pts) Express the following thermodynamic functions in SI units
   (a) $\alpha_p \quad 1/K$
   (b) $dq \quad J$
   (c) $P \quad \text{bar or Pa}$
   (d) $C_P \quad J/K$

11. (14 pts) Equilibrium.
   (a) Prove that
   \[ d(G/T) = -(H/T^2)dT + (V/T)dP \quad (5) \]
   (b) It is commonplace to see $ln K(T)$ plotted versus $1/T$. Derive the slope of this line.

   a) \[ d(G/T) = \frac{1}{T} dG - \frac{1}{T^2} G dT = -\frac{S}{T} dT - \frac{G}{T^2} dT + \frac{V dP}{T} \]
      \[ -S dT + V dP \]
      \[ d(G/T) = -\left( \frac{ST+G}{T^2} \right) dT + \frac{V dP}{T} = -\frac{H}{T^2} dT + \frac{V dP}{T} \]

   b) $\Delta G^0 = -RT \ln K$

   \[ d(\Delta G^0 / T) = -R d(ln K) = -\frac{H dT}{T^2} = +H d(1/T) \]

   \[ : d \ln K = -\frac{H}{R} d(1/T) \]

   \[ \text{slope of } \ln K \text{ vs } 1/T \text{ is } -\Delta H / R. \]