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

\( 1 \, \text{bar} = 10^5 \, \text{Pa} \quad 1 \, \text{L} = 0.001 \, \text{m}^3 \)

\[ \Delta U = C_v - F_{\text{ext}} \Delta V \]

\[ dU(S, V, n_i) = T \, dS - P \, dV + \sum_i \mu_i \, dn_i \]

\[ dH(S, P, n_i) = T \, dS + V \, dP + \sum_i \mu_i \, dn_i \]

\[ dA(T, V, n_i) = -S \, dT - P \, dV + \sum_i \mu_i \, dn_i \]

\[ dG(T, P, n_i) = -S \, dT + V \, dP + \sum_i \mu_i \, dn_i \]

\[ H = U + PV \]

\[ A = U - TS \]

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

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_v \]

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p \]

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

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

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

\[ P_1 V_1^3 = P_2 V_2^3 \quad T_2/T_1 = (V_1/V_2)^{\gamma - 1} \quad \text{adiabatic process} \quad \gamma = C_p/C_v \]

\[ H = -T \left( \frac{\partial G/T}{\partial T} \right)_P \]

\[ \left( \frac{\partial P}{\partial T} \right)_{\text{cyc}} = \begin{cases} \Delta H/T & \text{if} \quad \Delta V > 0 \\ \Delta H/T & \text{if} \quad \Delta V < 0 \end{cases} \]
1. (10 pts) One mole of water vapor at a temperature $T_1$ is heated to temperature $T_2 = 2T_1$. What are the changes in entropy and internal energy if a) the pressure is held constant; and b) the volume is held constant? Assume water vapor behaves as an ideal gas with $C_v = 3R$.

a) $dU = TdS - PdV$, $dH = TdS + VdP$

$dH = C_PdT = TdS \Rightarrow \Delta S = C_P \ln \left( \frac{T_2}{T_1} \right) = \frac{C_v}{R} \ln (2)$

$C_P = C_V + R = 4R$

$\Delta S = 4R \ln (2)$; $\Delta U = U_2 - U_1 = \Delta H - \Delta V$,

$\Delta U = 3R \ln (2)$

b) Constant volume, $\Delta U = C_V \Delta T = 3RT_1$

$TdS = C_V dT \Rightarrow \Delta S = C_V \ln \left( \frac{T_2}{T_1} \right) = 3R \ln (2)$

2. (10 pts) What changes in entropy and enthalpy occur when 25 mL of milk at 4°C are mixed with 300 mL of coffee at 95°C? Assume that the heat capacity of milk and coffee are the same with $C_v \approx C_p \approx 4.18 J/(K \cdot g)$.

$\Delta H = Q = 25(7-4) + 300(95-4) \Rightarrow 325 T = 100 + 300 \times 95$

$T = 88°C = 361 K$

Constant pressure process

$\Delta S = C_P \ln \left( \frac{T_C}{T_{milk}} \right) + \frac{C_P}{T_c} \ln \left( \frac{T_c}{T_{coffee}} \right)$

$= \left[ 25 \times \ln \left( \frac{361}{273} \right) + 300 \times \ln \left( \frac{361}{268} \right) \right] \frac{4.18 J}{9 \cdot K}$

$\Delta S = 8.59 \text{ J/K}$
3. (10 pts) Calculate the melting temperature of ice under a pressure change of 100 bar. Assume that the density of ice is 0.96 g/mL and liquid water is 1.00 g/mL. The heat of fusion of water is 6.00 kJ/mol. Conversion factors with SI units are given on the title page. Include the sign of the temperature change in your answer.

\[ \frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \cdot \Delta V} \Rightarrow \Delta T = \frac{\Delta P \cdot T \cdot \Delta V}{\Delta H} \]

\[ \Delta P = \frac{10^2 \text{kbar} \times 10^5 \text{Pa/kbar}}{1 \text{bar}} \]

\[ \Delta V = \left(1 \text{ mol} - \frac{m \text{ L}}{0.96 \text{ g/mol}}\right) \times 18 \text{ g/mol} \times \frac{10^{-6} \text{ m}^3}{\text{mL}} \]

\[ T = 273 \text{ K}, \quad \Delta H = 6 \times 10^3 \text{ J} \]

\[ \Delta T = \frac{(10^7)(273)(-0.75 \times 10^{-6})}{6 \times 10^3} = -0.341 ^\circ \text{C} \]

Depressed the freezing pt.

4. (10 pts) The Gibbs energy of a material at pressure P and temperature T is given by

\[ G(T, P, n) = n \left( RT \ln \left( \frac{P \lambda}{T \beta} \right) + b \right) \]

(1)

where \( b \) and \( \lambda \) are constants. Determine the heat capacity, \( C_v \), and the isothermal compressibility, \( \kappa_f \).

\[ V = \frac{\partial G}{\partial P} = \frac{nRT}{P} + nb \]

\[ \frac{\partial V}{\partial P} = -\frac{nRT}{P^2} \quad \Rightarrow \quad \kappa = \frac{nRT}{P^2V} = \frac{1}{\frac{1}{T} + \frac{bP}{nRT}} \]
7. (40 pts) Derive the following identities using as a starting point any of the relations given on page 1.

\[
\frac{C_v}{T} = \left( \frac{\partial S}{\partial T} \right)_V
\]

\[
dU = TdS - PdV = C_VdT + \left( \frac{\partial U}{\partial V} \right)_T dV
\]

\(\frac{\partial}{\partial T}\) const \(V\)

\(TdS = C_VdT \Rightarrow \left( \frac{\partial S}{\partial T} \right)_V = \frac{C_v}{T}
\]

\[
\left( \frac{\partial A}{\partial V} \right)_p = -P - \frac{S}{\alpha_p V}
\]

\[
dA = -SdT - PdV
\]

\[
\left( \frac{\partial A}{\partial V} \right)_p = - \left( \frac{\partial U}{\partial V} \right)_p S - P = -P - \frac{S}{\alpha_p V}
\]

but \(\left( \frac{\partial U}{\partial T} \right)_p = \alpha_p V\)
5. (8 pts)
(a) Circle the correct response from the list of equalities. For a one component, two phase system, it follows that

\[ A_1(T, V) = A_2(T, V); \quad G_1(T, P) = G_2(T, P) \]
\[ \mu_1(T, P) = \mu_2(T, P); \quad S_1(T, P) = S_2(T, P) \]

(b) Circle the false statement.

- \[ TdS \leq dq \]
- \[ dA|_{\text{constant}} \leq dv_{\text{lm}} \]
- If a system is at equilibrium at fixed T and P, G(T, P) has attained its minimum value.
- If a system is at equilibrium at fixed U and V, S(U, V) has attained its maximum value.

6. (12 pts) Draw \( C_v(T) \) vs \( T \) for argon assuming a) ideal gas behavior; and b) real fluid behavior close to the critical point. c) Define mathematically what is meant by a second order phase transition.

\[ C_v \]
\[ \lambda \text{ point transition @ } T = T_c \]
\[ \text{ideal gas behavior (no singularity)} \]

\[ \left( \frac{\partial^2 C_v}{\partial x^2} \right) \to \infty \quad x = T \text{ or } P \]
\[
\frac{\partial T}{\partial T} = \frac{TV \alpha_p}{C_p}
\]

(4)

\[dS = \left(\frac{\partial S}{\partial T}\right)_p dT - \left(\frac{\partial S}{\partial \rho}\right)_T d\rho \]

\[\frac{\partial \rho}{\partial T} = \frac{\partial \rho}{\partial \nu} \frac{\partial \nu}{\partial T}
\]

\Rightarrow \quad \frac{C_p}{T} \left(\frac{\partial T}{\partial \rho}\right)_s = \frac{\partial \nu}{\partial T}

\Rightarrow \quad \left(\frac{\partial T}{\partial \rho}\right)_s = \frac{TV \alpha_p}{C_p}

\[\left(\frac{\partial G}{\partial \nu}\right)_T = \frac{1}{\kappa_T}
\]

(5)

\[dG = -SdT + \nu d\rho
\]

\[\left(\frac{\partial G}{\partial \nu}\right)_T = \nu \left(\frac{\partial \rho}{\partial \nu}\right)_T = -\frac{1}{\kappa_T}
\]