

Lecture 21 (Final Exam Review)

Tuesday, November 26, 2024 10:00

Important: Final Exam Location

Mackinnon 304

Cumulative, but emphasis on second half of the course

Practice Problems

1. Why does the chemical potential change with pressure even if the system is incompressible (i.e. remains at the same volume when pressure is applied)?

Solution: $dw = -pdV$

$$du = Vmdp - SmdT$$

If $dT=0$, then $du = Vmdp$

V_m is the molar volume, $V_m \neq 0$

$dm > 0$, $dp < 0$

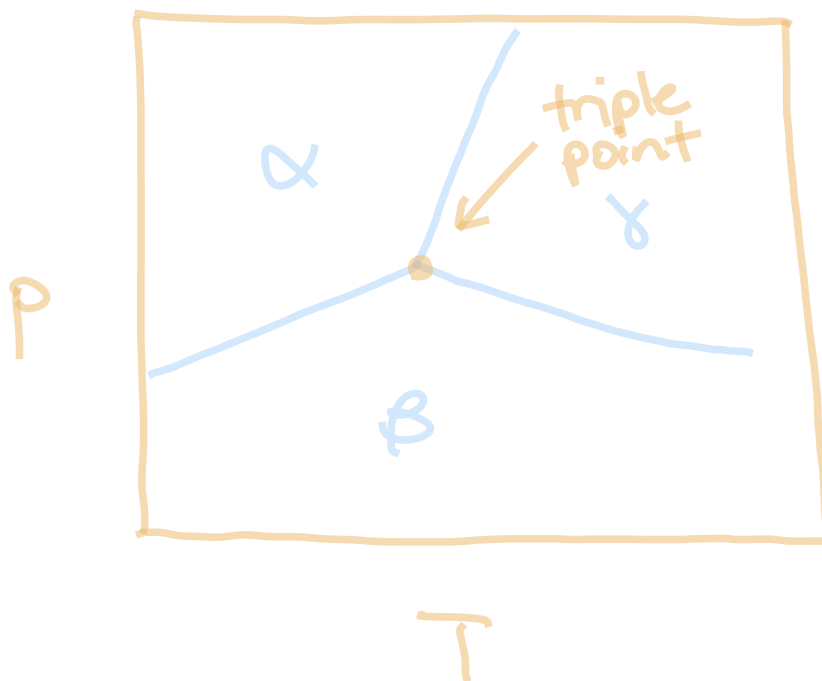
Alternatively: think about what is happening to the system physically.

A compressed system can transmit energy in the same way that a hydraulic fluid does. Furthermore, an incompressible system under pressure is under stress at a molecular level. Its bonds or intermolecular repulsive forces resist external forces without contraction

2. For a one-component system, draw a schematic labelled phase diagram given that at low T and low p , phases α and β are in equilibrium; as the temperature and pressure rise, there comes a

and pressure rise, there exists a point at which phases α , β , and γ are all in equilibrium; at high temperature and pressure, only phase γ is present; at low temperature and high pressure, only phase α is present. Comment on any special features of your diagram.

Solution :



3. Estimate the difference between the normal and standard boiling point of water. At the normal boiling point the enthalpy of vaporization of water is $40.7 \text{ kJ} \cdot \text{mol}^{-1}$. $\Delta_{\text{vap}} H$

Solution: "normal boiling point": T^*
 measured at $1 \text{ atm} = 101,325 \text{ Pa}$, p^*
 "standard boiling point": measured
 at $1 \text{ bar} = 100,000 \text{ Pa}$, p

Use the Clausius-Clapeyron equation:

$$\ln \frac{p}{p^*} = - \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

or, start from

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

$$\int_{p^*}^p d \ln p = \frac{\Delta_{\text{vap}} H}{R} \int_{T^*}^T \frac{1}{T^2} dT$$

$$\ln \frac{p}{p^*} = - \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

Back to the first equation

$$\ln \frac{p}{p^*} = - \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

$$\left(\frac{1}{T} - \frac{1}{T^*} \right) = - \frac{R}{\Delta_{\text{vap}} H} \ln \frac{p}{p^*}$$

$$\frac{1}{T} = \frac{1}{T^*} - \frac{R}{\Delta_{\text{vap}} H} \ln \frac{p}{p^*}$$

$$T = \frac{1}{\frac{1}{T^*} - \frac{R}{\Delta_{\text{vap}} H} \ln p/p^*}$$

$$T = \frac{1}{\frac{1}{373.15 \text{ K}} - \frac{8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}}{40,700 \text{ J} \cdot \text{mol}^{-1}}}$$

$$T = 99.63^\circ\text{C} = 372.78\text{ K}$$

Finally, $\Delta T = (100 - 99.63)^\circ\text{C}$

$$\Delta T = 0.37^\circ\text{C} \text{ or } \epsilon$$

4. Suppose that $n_A = 0.22 n_B$ and small change in composition results μ_A changing by $\delta\mu_A = -15\text{ J}\cdot\text{mol}^{-1}$

By how much will μ_B change?

Solution: $n_A d\mu_A = -n_B d\mu_B$

Gibbs-Duhem equation

$$\sum_J n_J d\mu_J = 0$$

Assume that going from infinitesimal to finite quantities is valid. $d\mu \rightarrow \delta\mu$

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$n_A d\mu_A = -n_B d\mu_B$$

$$n_A = 0.22 n_B$$

$$\frac{n_A}{n_B} = 0.22$$

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

$$= -(0.22) (-15 \text{ J}\cdot\text{mol}^{-1})$$

$$d\mu_B = +3.3 \text{ J}\cdot\text{mol}^{-1}$$

5. It is found that the normal boiling point of a binary solution of A and B with $x_A = 0.4217$ is 96°C . At this temperature the vapor pressure

At this temperature, the vapour pressure of pure A and pure B are 110.1 kPa and 76.5 kPa, respectively. Is this solution ideal?

Solution: If a solution is ideal, the vapour pressures of its components should follow Raoult's Law.

$$P_J = x_J P_J^*$$

$$P_A = x_A P_A^*$$

$$P_B = x_B P_B^*$$

$$P_A = (0.4217)(110,100) = 46.4 \text{ kPa}$$

$$P_B = (1 - 0.4217)(76,500) = 44.2 \text{ kPa}$$

$$P = P_A + P_B = (46.4 + 44.2) \text{ kPa}$$

$$P = 90.669 \text{ kPa}$$

normal boiling point, 101.325 kPa

Ideal solution vapour pressure is not close to atmospheric pressure.

The solution is not ideal.

6. For the equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ the degree of dissociation, α at 298 K is 0.201 at 1.00 bar total pressure. Calculate K .

Solution:	$\text{N}_2\text{O}_4(\text{g})$	$2\text{NO}_2(\text{g})$
initial	n	0
change	$-\alpha n$	$+2\alpha n$
equilibrium	$n - \alpha n$	

$$\begin{aligned} &= (1-\alpha)n \\ \text{mole} & \\ \text{fraction} & \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} \end{aligned}$$

$$= \frac{1-\alpha}{1-\alpha + 2\alpha}$$

$$= \frac{1-\alpha}{1+\alpha}$$

$$\begin{aligned} \text{partial} & \\ \text{pressure} & \\ (p_j = x_j p) & \left(\frac{1-\alpha}{1+\alpha} \right) p \end{aligned}$$

$$\begin{aligned} & 2\alpha n \\ & \frac{2\alpha n}{(1-\alpha)n + 2\alpha n} \end{aligned}$$

$$= \frac{2\alpha}{1+\alpha}$$

$$\left(\frac{2\alpha}{1+\alpha} \right) p$$

$$p = 1.00 \text{ bar}$$

$$K = \frac{a_{\text{NO}_2}^2}{a_{\text{N}_2\text{O}_4}}$$

$$= \frac{(P_{\text{NO}_2} / P^\ominus)^2}{P_{\text{N}_2\text{O}_4} / P^\ominus} = \frac{P_{\text{NO}_2}^2 / P^\ominus}{P_{\text{N}_2\text{O}_4} / P^\ominus}$$

$$K = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4} P^\ominus}$$

$$K = \frac{[2\alpha / (1+\alpha)]^2}{(1-\alpha) / (1+\alpha)}$$

$$= \frac{4\alpha^2 / (1+\alpha)^2}{(1-\alpha) / (1+\alpha)}$$

$$K = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)}$$

$$K = \frac{4(0.201)^2}{(1-0.201)(1+0.201)}$$

$$\boxed{1.1 - 1.18}$$

$$K = 0.100$$

7. The rate constant of a chemical reaction is found to double when the temperature is raised from 25°C to 35°C. Evaluate E_a .

Solution: $k = A e^{-E_a/RT}$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln k_2 - \ln k_1 = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{2k_1}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$E_a = +52.9 \text{ kJ} \cdot \text{mol}^{-1}$$