

This is a 70 min. exam. NO WRITING IS PERMITTED IN THE FIRST 10 MIN.  
You are allowed to use your class notes and one book of your choice.

1. Decide, with a justification, whether the following statements are true or false. [5 × 4 = 20]

- For a system composed of  $C$  components with chemical potential  $\mu_i$  for the  $i$ -th component and  $N_i$  is the number of moles of the  $i$ -th species,  $\sum_{i=1}^C \mu_i n_i$  will always have its smallest possible value.
- If a system has no constraints other than being in equilibrium with a constant pressure reservoir and constant temperature reservoir, then that system is in equilibrium if there is at least one process that increases its Gibbs energy.
- In a solution of water plus ethanol, each of the quantities  $\bar{V}_i$ ,  $\bar{S}_i$ , and  $\bar{G}_i$  is a function of  $T$ ,  $P$ , and  $x_{\text{H}_2\text{O}}$  and no other variables.
- If B is a component of a solution,  $\mu_B$  cannot be greater than  $\mu_B^*$ .
- The expression  $\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}$  is not applicable to solid-liquid transitions.

2. Trimethyl gallium,  $\text{Ga}(\text{CH}_3)_3$ , can be used as a feed gas to grow films of GaAs. Estimate the enthalpy of vaporization of  $\text{Ga}(\text{CH}_3)_3$  from the data of saturation pressure vs. temperature given in the table below.

$T(\text{K})$	250	260	270	280	290	310
$P^{\text{sat}} (\text{kPa})$	2.04	3.3	7.15	12.37	20.45	49.75

3. Starting from the compressibility factor,  $Z$ , for a van der Waals gas expressed in virial form, show that

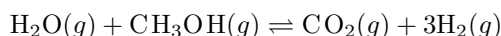
$$\ln \frac{f}{P} = \frac{bRT - a}{R^2 T^2} P + \frac{2abRT - a^2}{2R^4 T^4} P^2 + \dots$$

You are given that  $B' = \frac{B}{RT}$  and  $C' = \frac{C - B^2}{RT}$  where  $B'$  and  $C'$  are the first and second virial coefficients when it is a virial in  $P$  while  $B$  and  $C$  are the same coefficients when it is a virial in  $1/V$ . Note that  $(1 - x)^{-1} = 1 + x + x^2 + \dots$ .

4. Calcite and aragonite are two forms of solid calcium carbonate. The transition  $\text{CaCO}_3 (s, \text{calcite}) \rightleftharpoons \text{CaCO}_3 (s, \text{aragonite})$  is of special interest as a geobarometer. For this transition, at 25 °C,  $\Delta_{\text{rxn}} G^\circ = +1393 \text{ J mol}^{-1}$  and  $\Delta_{\text{rxn}} S^\circ = -3.72 \text{ J K}^{-1} \text{ mol}^{-1}$ . Calcite is hexagonal with a density of  $2.710 \text{ g cm}^{-3}$ , whereas aragonite is orthorhombic with a density of  $2.944 \text{ g cm}^{-3}$ .

- How many degrees of freedom does the calcite-aragonite equilibrium system have?
- Justify whether aragonite is a stable phase at  $P = 1 \text{ atm}$  and 25 °C.
- Can calcite and aragonite coexist in equilibrium under any conditions at 25 °C?

5. Fuel cells provide an attractive alternate energy source. Consider a fuel cell based on the direct conversion of methanol to form hydrogen:



This reaction, initially containing only 2 moles of water and 1 mole of methanol, is carried out at low pressure.

- What is the equilibrium extent of the reaction at 25 °C?
- What is the equilibrium extent of the reaction at 60 °C?
- How many moles of  $\text{H}_2$  can be produced per mole of  $\text{CH}_3\text{OH}$  in the feed?
- Write an expression for the Gibbs energy of the reaction mixture at equilibrium in terms of the chemical potentials.

	$\text{CO}_2$	$\text{CH}_3\text{OH}$	$\text{H}_2\text{O}$
$\Delta_f H^\circ (\text{kJ mol}^{-1})$ at 298 K	-393.5	-200.7	-241.8
$\Delta_f G^\circ (\text{kJ mol}^{-1})$ at 298 K	-394.4	-162.0	-228.6