

1. For a reversible reaction $A \xrightleftharpoons[k_{-1}]{k_1} Y + Z$
- The rate constants k_1 and k_{-1} can be measured by the T-jump technique. Show that the relaxation time is $\tau^* = \frac{1}{k_1 + 2k_{-1}x_e}$
- where x_e is the concentration of Y and Z at equilibrium. (14%)
2. Show that $\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$ (10%)
3. The solubility of $AgCl$ in water at $25^\circ C$ is $1.274 \times 10^{-5} \text{ mol dm}^{-3}$. On the assumption that the Debye-Hückel Limiting Law applies,
- (a) Calculate ΔG° for the process $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$.
- (b) Calculate the solubility of $AgCl$ in a mixed solution of $0.002M \text{ Ca(NO}_3)_2$ and 0.002 NaNO_3 . (12%)
4. A sample of sucrose ($C_{12}H_{22}O_{11}$) weighing $0.1328g$ is burned to completion in a bomb calorimeter at $25^\circ C$, and 2.186 kJ of heat are evolved. Calculate ΔU_m and ΔH_m for the combustion of sucrose. (10%)
5. A liter of water at $20^\circ C$ (density = 0.998 g cm^{-3}) is broken up into a spray in which the droplets have an average radius of 10^{-5} cm . The surface tension of water at $20^\circ C$ is $7.27 \times 10^{-2} \text{ Nm}^{-1}$. (a) Calculate the Gibbs energy change when the droplets are formed. (b) Calculate the ratio between the vapor pressure of the droplet and the vapor pressure of water at a plane surface. (12%)
6. Determine the number of degrees of freedom for the following systems?
- (a) Ice in a solution of water and alcohol.
- (b) $NH_4Cl(s)$ is allowed to dissociate to $NH_3(g)$ and $HCl(g)$ until equilibrium is reached.
- (c) CO , CO_2 , H_2 , and H_2O in equilibrium in the gas phase. (12%)
7. (a) What is azeotrope and how to break azeotropes? (6%)
- (b) What is Boyle temperature? (4%)
- (c) Describe the meanings of the two terms, $\frac{a}{V_m^2}$ and b , in van der Waals equation. (6%)
- (d) For a gas system from state 1 to state 2, the expansion work done on the surroundings through an irreversible process is smaller than that through a reversible process. Where does the lost work go? (4%)
- (e) Under what conditions do positive and negative deviations from Raoult's law occur? (4%)
- (f) Criteria for phase equilibrium (6%)

Note: $R = 8.314 \text{ J mol}^{-1} K^{-1}$