

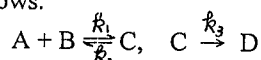
$$R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1} = 8.315 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} = 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$$

1. (a) For closed systems involving only pressure-volume work, show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - \kappa P}{\kappa}, \text{ in which } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \text{ and } \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T.$$

- (b) How does the internal pressure of a van der Waals gas depend on the molar volume? (13%)

2. Consider a liquid phase reaction  $A + B \rightarrow D$ , the mechanism is expressed as follows.



- (a) Derive the rate law using the steady-state approximation to eliminate the concentration of C. (5%)  
 (b) Assuming that  $k_3 \ll k_2$ , express the pre-exponential factor  $A$  and activation energy  $E_a$  for the apparent second-order rate constant in terms of  $A_1$ ,  $A_2$ , and  $A_3$  and  $E_{a1}$ ,  $E_{a2}$ , and  $E_{a3}$  for the three steps. (8%)

3. For the reaction  $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ , the dissociation pressures of  $\text{CaCO}_3(\text{s})$  versus temperature are shown as Figure 1.

- (a) How many degrees of freedom are there in the regions of I, II, and III? State the phases in each region.  
 (b) Estimate the value of  $\Delta G^\circ$  at 1000 K. (13%)

4. Water is vaporized reversibly at 100 °C and 1.013 bar. The heat of vaporization is 40.69 kJmol<sup>-1</sup>. (a) What are values of  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta G$ , and  $\Delta S$  for the water? (b) What is the value of  $\Delta S$  for the water plus the heat reservoir at 100 °C? (15%)

5. The standard electromotive force of the cell  $\text{Pt} | \text{H}_{2(\text{g})} | \text{HCl}_{(\text{al})} | \text{AgCl}_{(\text{s})} | \text{Ag}$  has been determined from 0 to 90 °C and may be represented by

$$\frac{E^\circ}{V} = 0.23659 - 4.8564 \times 10^{-4} \left(\frac{t}{^\circ\text{C}}\right) - 3.4205 \times 10^{-6} \left(\frac{t}{^\circ\text{C}}\right)^2 + 5.869 \times 10^{-9} \left(\frac{t}{^\circ\text{C}}\right)^3$$

- What are (a) the half-cell reactions, (b) the cell reaction, (c)  $\Delta G^\circ$ ,  $\Delta S^\circ$ ,  $\Delta H^\circ$ , and  $\Delta C_p^\circ$  for the cell reaction? (15%)

6. As shown in Figure 2, the Carnot heat engine for an ideal gas consists of the following steps: (1) Reversible isothermal expansion of the gas from state A to state B; (2) Reversible adiabatic expansion of the gas from state B to state C; (3) Reversible isothermal compression of the gas from state C to state D; (4) Reversible adiabatic compression of the gas from state D to state A. (15%)

- (a) What is the thermodynamic efficiency of the engine?  
 (b) What are  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  for each step?

7. The following table gives the volume of nitrogen (reduced to 0 °C and 1 bar) adsorbed per gram of active carbon at 0 °C at a series of pressures: (16%)

$P/\text{Pa}$	524	1731	3058	4534	7497
$v/\text{cm}^3 \text{ g}^{-1}$	0.987	0.34	5.08	7.04	10.31

- (a) Plot the data according to the Langmuir isotherm, and determine the constants.  
 (b) Calculate the surface area per gram of the active carbon if each nitrogen molecule occupied  $16.2 \times 10^{-20} \text{ m}^2$ .

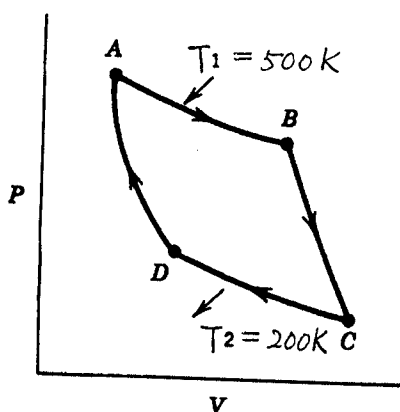


Figure 2

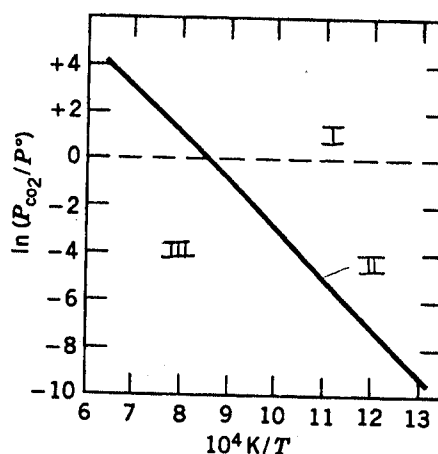


Figure 1