九十五學年度資格考

化工熱力學

1. (15%) (a) Usually, when salts dissolve in water, the solution becomes warm. Such a process is exothermic. When other salts, such as sodium chloride, dissolve in water, the solution becomes cold, indicating an endothermic process. Since endothermic processes are usually not spontaneous, why does the latter process proceed?

   (b) Which of the following thermodynamic quantities are state functions? Explain. (i) work, (ii) entropy, (iii) enthalpy, (iv) free energy. Also explain the difference between the differential of a state function and a non-state function.

   (c) Adenosine triphosphate (ATP) plays an important role within living cells. The hydrolysis of ATP immediately and directly provides the free energy to drive an immense variety of endergonic biochemical reactions, an example is given as followed.

   $ATP \rightarrow ADP + P_i \qquad \Delta G_0 = -7.3 kcal/mol$

   $Glucose + P_i \rightarrow glucose\text{-}6\text{-}phosphate \; \Delta G_0 = +3.3 kcal/mol$

   What factors make ATP suitable as an "energy currency" for the cell?

2. (15%) What is the definition of the third law of thermodynamics? The Trouton rule says that entropy change for a pure fluid changing from liquid to gas at its boiling point ($\Delta S = \lambda / T$, λ = evaporation heat, T = boiling point) is near the same at about 85 J/(mol·K) in spite of different fluids. From the microscopic viewpoint of entropy, i.e., $S = k \ln \Omega$, please explain the meaning of the Trouton rule.

3. (20%) **(a)** Starting from the differential form of energy balance for a homogeneous closed system $d(U) = dQ + dW$ (where U = internal energy, Q = heat, W = work) and the definition of enthalpy $H = U + PV$ (where P = pressure and V = volume), show that the differential form of entropy change of an ideal gas is $dS = C_P^{ig} \frac{dT}{T} - R\frac{dP}{P}$. (where C_P^{ig} is the ideal gas heat capacity and R is the gas constant).

   (b) A stream of 2 mol/s of air goes from 1000 K and 10 bar to 500 K and 5 bar while doing 5.0 kW of work. Surrounding are 300 K and 1 bar. (see Fig. 1) What is the lost work for this process? (with negligible changes in kinetic and potential energies, for air C_P^{ig} = 29.1 J/mol·K, R = 8.314 J/mol·K) (6%)

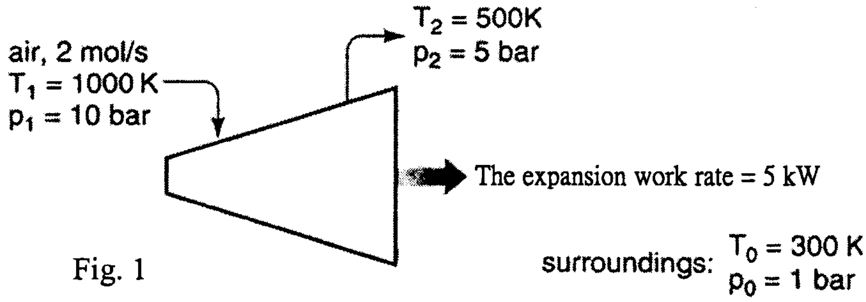


Fig. 1

4. (15 %)

(a) Show that the conditions for vapor liquid-equilibrium at constant N (number of moles), T, and V are $\underline{G}^V = \underline{G}^L$ and $P^V = P^L$, where $\underline{G}^V$ and $\underline{G}^L$ are Gibbs free energies per mole of vapor and liquid, respectively.

(b) Show that the condition for vapor-liquid equilibrium at constant N, T, and P is $\underline{G}^V = \underline{G}^L$.

5. (15 %) Air (assumed to be an ideal gas with $C_P = 29.3$ J/mol K) enters a throttling valve at 35 bar and 600 K and left at 7 bar. Assuming there is no heat loss from the valve, what is the exit temperature of the air and its change in entropy?

6. (20 %) One gram mole of a gas at a temperature of 25℃ and a pressure of 1 bar (the initial state) is to be heated and compressed in a frictionless piston and cylinder to 300℃ and 10 bar (the final state). Compute (a) the heat and work required and (b) ΔS (entropy change) along each of the following paths:

Path A: Isothermal (constant temperature) compression to 10 bar, and then isobaric (constant pressure) heating to 300℃.

Path B: Isobaric heating to 300℃ followed by isothermal compression to 10 bar.

For simplicity, the gas is assumed to be ideal with $C_P = 38$ J/mol K.

Thermodynamic functions

$$d\underline{U} = T\,d\underline{S} - P\,d\underline{V} = C_V\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]d\underline{V}$$

$$d\underline{H} = T\,d\underline{S} + \underline{V}\,dP = C_P\,dT + \left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right]dP$$

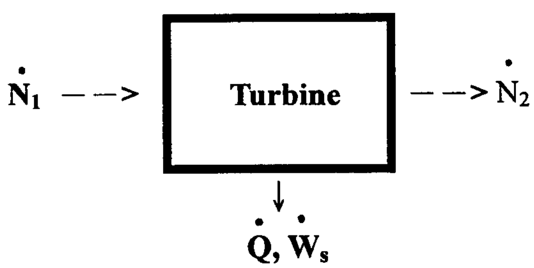
$$d\underline{A} = -P\,d\underline{V} - \underline{S}\,dT, \quad dA = -P\,dV - S\,dT + \underline{G}\,dN$$

$$d\underline{G} = \underline{V}\,dP - \underline{S}\,dT, \quad dG = V\,dP - S\,dT + \underline{G}\,dN$$

2007 Ph.D. Qualifying Examination

Advanced Chemical Engineering Thermodynamics

1. (25%) A fluid flow engine (turbine) involves the expansion of a high-pressure, high temperature fluid through a nozzle to obtain a low-pressure, high-velocity gas. This gas then impinges on turbine blades where the kinetic energy of the gas is transformed to the turbine rotor, and thus is available as shaft work. The resulting low-pressure, low-velocity gas leaves the turbine. The kinetic and potential energy changes of the fluid entering and leaving the device cancel or are negligible and the heat flow $\dot{Q}$ can be identified as occurring at a single temperature T. **First, make steady-state mass, energy, and entropy balances for such heat engines and then solve these equations for $\dot{Q}$ and the work flow $\dot{W}_s$. What is the maximum rate at which work can be obtained from such an engine?**



2. (25%) A Carnot or other engine (e.g., air conditioners) can be operated in reverse so that mechanical energy (work) is used to pump heat from a low-temperature source to a high-temperature sink. Air conditioners are now used for both winter heating (by pumping heat from the surroundings to the house) and summer cooling (by pumping heat from the house to the surroundings). The coefficient of performance for a heat pump is defined as the ratio of the heat flow from the low-temperature source to the work required to produce that flow. The heat supplied to the high-temperature sink is the sum of the heat and work flows. Consider a heat pump that uses a lake as a heat source in the winter and as a heat sink in the summer. The house is to be maintained at a winter temperature of 65 °F and a summer temperature of 78 °F. To achieve this efficiently, the indoor coil temperature should be 100 °F in the winter and 40 °F in the summer. The outdoor coil temperature is 40 °F in the winter and 65 °F in the summer. **Starting from energy and entropy balances, compute the coefficients of performance for a Carnot cycle heat pump for winter and for summer operation.**

3. (15%) The following data are available for water (P in Pa, T in K):

$$\ln P^{sub}(ice) = 28.8926 - 6140.1/T$$

$$\ln P^{vap}(water) = 26.3026 - 5432.8/T$$

where P^{sub} is the sublimation pressure, and P^{vap} is the vapor pressure.

(a) Compute the triple-point temperature and pressure of water.

(b) Compute the heat of vaporization, the heat of sublimation, and the heat of fusion of water at its triple point.
Gas constant $R = 8.314$ J/(mol K)

4. (15%) *Charles' law* states that, for a gas at low pressures, the volume of the gas is directly proportional to the temperature at constant pressure. *Boyle's law* states that, for a gas at low pressures, the pressure of the gas is inversely proportional to the volume at constant temperature. Derive the ideal-gas law from these two observations.

5. (20%) If 2 kg of liquid water at 90°C is mixed adiabatically and at constant pressure with 3 kg of liquid water at 10°C, what is the total entropy change resulting from this process? For simplicity, assume the heat capacity of water to be constant at C_P = 1 cal/(g K) or 4184 J/(kg K).