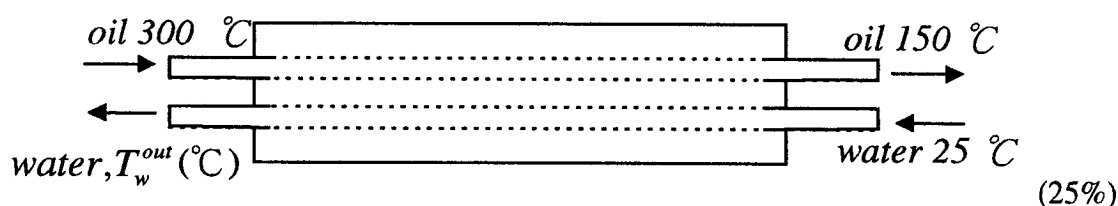


九十二學年度資格考

化工熱力學

1. A heat exchanger for cooling a hot hydrocarbon liquid uses 10 kg/min of cooling H₂O which enters the exchanger at 25 °C. Five kg/min of hot oil enters at 300 °C and leaves at 150 °C and has an average specific heat of 2.51 kJ/kg-K.

- (i) Demonstrate that the process is irreversible as it operates now;
 (ii) Assuming no heat losses from the exchanger, calculate the maximum work which could be obtained if we replaced the heat exchanger with a Carnot device which replaced the water stream and transferred heat to the surroundings at 25 °C.



2. (i) Start from $dG = -SdT + VdP$ to show $\left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P = H$. (ii) Since we are concerned with changes in the standard-state Gibbs energy, the condition of constancy of pressure is satisfied by the definition of the standard state. Please show the relation between the equilibrium constant (K) for a chemical reaction and the reaction temperature (T). (iii) A fuel cell applying a reaction between hydrogen and oxygen as $H_2 + \frac{1}{2}O_2 = H_2O$ which has standard formation change of enthalpy and free energies as $\Delta H^0 = -241.82 \text{ kJ/mol}$ and $\Delta G^0 = -228.57 \text{ kJ/mol}$, respectively. For a high temperature typed fuel cell that operates at high temperatures. (iii) Please use the heat capacity (C_p (J/mol·K)) data given below to calculate the equilibrium constant at 1000 K.

$$C_p = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$$

	a_0	a_1	a_2	a_3	a_4
H ₂	2.991423	7.000644 $\times 10^{-4}$	-5.633828 $\times 10^{-8}$	-9.231578 $\times 10^{-12}$	1.582752 $\times 10^{-15}$
O ₂	3.697578	6.135197 $\times 10^{-4}$	-1.258842 $\times 10^{-7}$	1.775281 $\times 10^{-11}$	-1.136435 $\times 10^{-15}$
H ₂ O	2.672145	3.056293 $\times 10^{-3}$	-8.730260 $\times 10^{-7}$	1.200996 $\times 10^{-10}$	-6.391618 $\times 10^{-15}$

(25%)

3. Using the Jacobians transformation method shows that

$$C_p - C_v = -T \left(\frac{\partial P}{\partial T} \right)_v^2 \left(\frac{\partial V}{\partial P} \right)_T \quad (10 \%)$$

Note that: $dU = TdS - PdV$, $H = U + PV$, $G = H - TS$, and
Maxwell relationship: $J(T, S) = J(P, V)$

4. The Kihara potential function for spherical molecules is defined as

$$\Gamma = \begin{cases} \infty & \text{for } r < 2a \\ 4\epsilon \left[\left(\frac{\sigma - 2a}{r - 2a} \right)^{12} - \left(\frac{\sigma - 2a}{r - 2a} \right)^6 \right] & \text{for } r \geq 2a \end{cases}$$

- (a) Sketch qualitatively the Kihara potential function. Mark the parameters, a , σ , and ϵ on the graph. (5 %)
- (b) What are the physical meanings for the parameters, a , σ , and ϵ , respectively? (5 %)
- (c) Why is the Kihara potential function more appropriate than the Lennard-Jones potential function for real molecules? (5 %)
5. (a) List all types of intermolecular forces, which may exist in the following mixtures:
- (M1) water + methanol
- (M2) n-heptane + n-octane
- (M3) toluene + 1,2,4-trichlorobenzene (9 %)
- (b) Based on your knowledge of intermolecular forces, compare qualitatively the magnitudes of enthalpy change of mixing of the above three mixtures through an equal molar mixing. Give any explanation to support your answer. (6 %)
6. Wilson developed the well-known Wilson activity coefficient model on the basis of local composition concept. Please describe briefly the concept of "local composition". (10 %)