Close book

1. (20%) Question (True or False) and explanation,

(1) The first law of thermodynamics requires that the total energy of any system be conserved within the system.

(2) The heat capacity at constant pressure of a single-component system consisting of liquid and vapor in equilibrium is infinite.

(3) For any gas at constant temperature, the product PV approaches zero as the pressure approaches zero.

(4) For a closed gaseous system, the value of \(- \int P \, dV\) for the change of the gas from one given state to another is independent of the path so long as all processes are reversible.

(5) If a system undergoes a process during which its entropy does not change, the process is reversible and adiabatic.

2. (20%) A rigid tank of 0.3 m³ capacity, contains water as saturated liquid and vapor at 15 bar. If 99% of the water mass is liquid, how much heat must be added before the tank just becomes full of liquid. (Use steam table)

3. (20%) Calculate the minimum amount of work required to produce 1 kg of ice in a flow process starting with water at 30°C. Assume the surroundings to be 30°C. (Heat of fusion of water 333.9 J/g, Heat capacity of water 4.18 J/g-K)

4. (20%) 
   (a) 1 kg of liquid water initially at 100°C mixed with 1 kg of liquid water initially at 0°C, calculate the entropy change of hot water, cold water and the total process.
   (b) If the heat flux from hot water (1 kg, 100°C) to cold liquid water (1 kg, 0°C) can supply a Carnot engine, calculate the maximum work obtainable. (Heat capacity of water 4.18 J/g-K)

5. (20%) You are on the supermarket to shop "the energy cylinder". The well-insulated energy cylinders contain air at different temperature and pressure with different prices tags (Figure). Cylinder of gas may be connected to any work-producing devices (Carnot engine, expansion turbine, ...) or any combination of such devices to generate work. Derive the necessary equations for the unit cost of work energy (e.g. $/J oule), and pick up the best buy among three cylinders. Assume air is an ideal gas, and the ambient temperature and pressure are 300K and 1 atm. (air \(C_v = 20.7\) J/mol-K, \(C_p = 29.0\) J/mol-K)

\[
\begin{array}{c|c|c}
\text{Volume} & \text{Temperature} & \text{Pressure} \\
\hline
1 \text{ m}^3 & 400 K & 8 \text{ atm} \\
0.1 \text{ m}^3 & 800 K & 36 \text{ atm} \\
0.2 \text{ m}^3 & 600 K & 33 \text{ atm} \\
\end{array}
\]

\$400
\$125
\$300

Gas constant : \(R=82.06 \times 10^{-6} \text{ m}^3\text{-bar/mole-K}, \) or \(R=8.314 \text{ j/mole-K}\)
The Second Midterm of Thermodynamics (Class 3)

12/9/2000
10:10 ~ 12:00

Close book

1. Derive two equations, (a) \( dS = \frac{C_v}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V dV \), (b) \( dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP \)

2. Methane steam reforming is one way to produce synthesis gas (primarily CO and H\(_2\)). The reaction is shown as,

\[
\text{CH}_4 (g) + \text{H}_2\text{O} (g) \rightarrow \text{CO} (g) + 3 \text{H}_2 (g) \Delta H_{298K}^0 = 49237 \text{ cal}
\]

The reactants are preheated to 600K, and the final products are at 1300K. Calculate the heat requirement if the reaction is completed.

\[
C_p^o = a + b T + c T^2 + d T^3, \quad [\text{cal/mole}], \quad T [\text{K}]
\]

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>4.75</td>
<td>0.200E-2</td>
<td>0.30E-5</td>
<td>-2.63E-9</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>7.70</td>
<td>0.046E-2</td>
<td>0.25E-5</td>
<td>-0.86E-9</td>
</tr>
<tr>
<td>CO</td>
<td>6.73</td>
<td>-0.040E-2</td>
<td>0.13E-5</td>
<td>-0.53E-9</td>
</tr>
<tr>
<td>H(_2)</td>
<td>6.95</td>
<td>-0.046E-2</td>
<td>0.095E-5</td>
<td>-0.21E-9</td>
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</tbody>
</table>

3. (a) Starting with the Clausius inequality show that \( \Delta A_{t,v} \leq 0 \) for a spontaneous process. (b) write the corresponding equilibrium criteria and apply it to a single-component two-phase system in equilibrium to obtain the conditions of equilibrium.

4. Gas HFC-134a at 60 bar and 100°C is throttled adiabatically (isenthalpic) to a pressure 1 bar. What is its final temperature? If it becomes two phases, what is the fraction of liquids? How are the entropy (kJ/kg•K) and enthalpy (kJ/kg) changes of gas phase?

5. The melting point of benzene is found to increase from 5.50 to 5.78°C when the external pressure is increased by 100 atm. The heat of fusion of benzene is 30.48 cal/g. What is the change of volume per gram accompanying the fusion of benzene?

\[
\begin{align*}
dU &= TdS - PdV \\
dH &= TdS + VdP \\
dA &= -PdV - SdT \\
dG &= VdP - SdT
\end{align*}
\]

Clausius inequality : \( \Delta U - T \Delta S - W \leq 0. \)

Clapeyron equation : \( \frac{dP}{dT} = \frac{h^\alpha - h^\beta}{(v^\alpha - v^\beta)T} \)

Gas constant \( R = 82.06 \times 10^{-6} \text{ m}^3\text{-bar/mole-K} \)

\( R = 8.314 \text{ j/mole-K} \)

1 cal = 4.18 joule
The Final Exam of Thermodynamics (Class 3)

1/9/2001          10:0 ~ 12:00  AM

Close book

1. Compounds A and B are members of the same chemical family and have the following vapor pressures.

<table>
<thead>
<tr>
<th>t (°F)</th>
<th>P_A° (mmHg)</th>
<th>P_B° (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>600</td>
<td>500</td>
</tr>
<tr>
<td>200</td>
<td>1000</td>
<td>950</td>
</tr>
</tbody>
</table>

Assume that these compounds form ideal solutions. Calculate the vapor mol fraction of A and the total pressure for VLE when the liquid mole fraction of A is 0.500 and the temperature is 175°F.

2. An azeotrope occurs in the A-B system but the only information that is known is the temperature (366 K) and pressure (1 atm). The vapor pressure of A and B at 366 K are 700 and 600 mmHg, respectively. Calculate the azeotrope composition at 366 K. Use the Margules equation with A_{12}=A_{21}.

3. Suppose for a given T and P that the composition dependence of the liquid molar volume for a particular binary system is given by,

\[ V = 100 x_1 + 80 x_2 + 2.5 x_1 x_2 \]  

[cm³/mole]

(a) Derive the corresponding expressions for \( \bar{V}_1 \) and \( \bar{V}_2 \), i.e. partial molar volume; (b) verify with Gibbs-Duhem equation.

4. Calculate \( \Delta H \) and \( \Delta G \) at 1000°C for the water-gas-synthesis reaction,

\[ C (s) + H_2O (g) = CO (g) + H_2 (g) \]

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>( \Delta H_f^0 )</th>
<th>( \Delta G_f^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (s)</td>
<td>14.72</td>
<td>6.41</td>
<td>-7.21</td>
<td></td>
<td></td>
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<tr>
<td>H_2O (g)</td>
<td>28.85</td>
<td>12.06</td>
<td>1.01</td>
<td>-241.818</td>
<td>-228.572</td>
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<tr>
<td>CO (g)</td>
<td>28.07</td>
<td>4.63</td>
<td>-0.26</td>
<td>-110.525</td>
<td>-137.169</td>
</tr>
<tr>
<td>H_2 (g)</td>
<td>27.01</td>
<td>3.51</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Heat capacity : \( C_p = a + b \times 10^{-3} T + \frac{c \times 10^5}{T^2} \)  

[j/mole-K], \( \Delta H_f^0 \) and \( \Delta G_f^0 \) [kJ/mole] are at 298 K and 1 atm.

5. The decomposition reaction of A is shown as following,

\[ A = B + C \]

The reaction is carried out in liquid phase at 60°C. The reaction equilibrium constant is 2. The saturated vapor pressures of A, B and C are 6, 10 and 8 atm at 60°C, respectively. Liquids A and C form an ideal solution. Liquid B is immiscible in the (A+C) solution. Assume ideal gas behavior of vapor phase. Calculate the vapor compositions and the equilibrium pressure of this system at 60°C.

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Margules equation: \( \ln \gamma_1 = X_2^2 \left[ A_{12} + 2 (A_{21} - A_{12}) X_1 \right] \), \( \ln \gamma_2 = X_1^2 \left[ A_{21} + 2 (A_{12} - A_{21}) X_2 \right] \)

General Gibbs-Duhem equation : \( \left[ \sum n_i d\mathcal{M}_i = 0 \right]_{T,P} \), \( \Delta G^o = -RT \ln K \)

Clausius-Claypeyron Eqn. \( \ln p^o = c - \frac{\Delta h}{RT} \), \( \frac{d(ln K)}{dT} = \frac{\Delta H^o}{RT^2} \)

Gas constant \( R=1.987 \) cal/mole-K, or 8.314 j/mole-K, 1 cal = 4.18 joule