The First Midterm of Thermodynamics (Class 2)

10/23/2001
10:00 ~ 12:00

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1. (20%) Questions (True or False) and explanations,

(1) The entropy of an ideal gas is a function of temperature only. Why?
(2) The energy of an isolated system must be constant. Why?
(3) The entropy of an isolated system must be constant. Why?
(4) The heat capacity at constant volume of a single-component system consisting of liquid and vapor in equilibrium is infinite. Why?
(5) If a system undergoes an irreversible change from an initial equilibrium state i to final state f, the entropy change of the surroundings must be less than it would be if the system changed from i to f reversibly. Why?

2. (20%) One kg of steam contained in a horizontal frictionless piston and cylinder is heated at constant pressure of 1.013 bar from 125°C to such a temperature that its volume doubles. Calculate the amount of heat that must be added to accomplish this change, the final temperature of the steam, and the work the steam does against its surroundings. (Use steam table)

3. (20%) Joe claims to have invented a steady-state flow device in which the inlet is steam at 300°C and 5 bar, the outlet is steam at 100°C and 1 bar. The device is adiabatic and produces approximately 388 kJ work per kg of steam passed through. Should we believe his claim? Check both the 1st and 2nd laws. (Use steam table)

4. (20%) An ideal gas of constant heat capacity \([C_p = 30 \text{ J/(mole K)}]\) at 10 bar and 295 K enters a Ranque-Hilsch vortex tube. Two equal amount of steam leave vortex tube at 1 bar adiabatically. Determine the maximum temperature spread obtainable?

5. (20%) Air flowing at the rate of 1 kmol/min enters a compressor at 1 bar and 294.4 K and leaves at 10 bar and 405.4 K. Cooling water flows through the cooler inside compressor at the rate of 1 kg/sec, and its temperature increases 15.6 K. (\text{1996})

(a) How much power \((W_s)\) is supplied to the compressor? (in Watt)
(b) If compressor is operate reversibly, with the same inlet and out conditions of air, calculate the power requires to attain the same change in state of the air. Is the power less than that of (a)? Why? Make any necessary assumptions.

Assume air is an ideal gas, \(C_p = 30 \text{ J/(mole K)}\)

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Gas constant: \(R = 82.06 \times 10^{-6} \text{ m}^3\text{-bar}/\text{mole-K},\) or \(R = 8.314 \text{ J/mole-K}\)

1 cal = 4.184 joule
1. Starting from $S(T,V)$ and $H(T, V)$, first derive two equations,
   (a) $dS = \frac{C_v}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$; (b) $dH = [C_v + V(\frac{\partial P}{\partial T})_V]dT + [T(\frac{\partial P}{\partial T})_V + V(\frac{\partial P}{\partial V})_T]dV$, then specify the type of experiment data required to calculate $\Delta S$ and $\Delta H$.

2. A gas is cooled by state-steady throttling process. High-pressure gas at 360 K and 30 atm will pass through a well-insulated throttle valve to a pressure of 1 atm. Estimate the temperature of the low pressure gas. (Hint: use corresponding state method)
   Data: $C_p = 7$ cal/mole, $T_c = 300$ K, $P_c = 30$ atm.

3. The following data are available for water
   \begin{align*}
   \ln P_{\text{sub}(\text{ice})} &= 28.8926 - 6140.1/T \\
   \ln P_{\text{vap}(\text{water})} &= 26.3026 - 5432.8/T \\
   \end{align*}
   (a) Compute the triple point temperature and pressure of water.
   (b) Compute the heat of evaporation, sublimation and fusion of water at its triple point.

4. Two substances, A and B, form an ideal solution and have the following vapor pressures at 330 K.
   \begin{align*}
   P_0^A &= 900 \text{ mm Hg} \\
   P_0^B &= 800 \text{ mm Hg} \\
   \end{align*}
   For a mixture, total mole fraction of A, $z_A = 0.3$, (a) what is the bubble point pressure? (b) what pressure is necessary for complete evaporation.

5. There are several possible expressions that can be used for the Gibbs excess free energy, One of them is
   \[ G^e = x_1 x_2 [A + C (x_1 - x_2)^2] \] (unit : j/mole)
   Find expressions for the activity coefficient which $\gamma_i$ is given solely in terms of $x_2$, A and C, $\gamma_2$ only in terms of $x_1$, A an C. [Hint : $RT \ln \gamma_i = \left(\frac{\partial G^e}{\partial N_i}\right)_{T,P,n_i}$]
1. A 20 wt% solution of sulfuric acid in water is to be enriched to a 60 wt% sulfuric acid solution by adding pure sulfuric acid. (a) How much pure sulfuric acid should be added in 1 kg of 20 wt% solution? (b) If the 20 wt% solution is available at 21.1°C, and pure sulfuric acid at 0°C, how much heat will have to add or remove to produce the 60 wt% solution at 65.6°C. (c) How much heat will have to add or remove to make this 60 wt% solution at its boiling point? (use Figure)

2. At 80°C, compounds A and B each have a vapor pressure of 800 mm Hg. At this temperature the A-B system forms an azeotrope containing 50 mol% of A at total pressure of 1050 mm Hg. Compound A has a heat of vaporization of 8000 cal/mole and B has a heat of vaporization of 10000 cal/mole. Estimated the azeotrope compositions and total pressure at 60°C. For activity coefficients, use the Margules equation with $A_{12} = A_{21}$. (hint: use Clausius-Claypeyron Eqn. to calculate saturated pressure at 60°C)

3. The partial molar enthalpies of species in simple binary mixtures can be sometimes be approximated by the following expression,

$$H_1 = a_1 + b_1 x_2^2$$

$$H_2 = a_2 + b_2 x_1^2$$

(a) For these expression show that $b_1 = b_2$, (b) Making use of the fact that $\lim_{x_i \to 1} \bar{\theta}_i = \theta_i$, for any thermodynamic property $\theta$, show that $a_1 = H_1$, $a_2 = H_2$, and $\Delta H_{\text{mix}} = b_1 x_1 x_2$. (hint: use Gibbs-Duhem equation)

4. One of air pollution, NO, may be generated from boiler by the following reaction. Assume air contains 21 mole% O$_2$ and 79 mole% N$_2$, calculate the equilibrium compositions at 1500 K and 1 atm. (that is, mole fractions of NO, N$_2$ and O$_2$ at equilibrium)

$$\frac{1}{2} \text{N}_2 (g) + \frac{1}{2} \text{O}_2 (g) = \text{NO (g)}$$

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
<th>$\Delta H^0$</th>
<th>$\Delta G^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ (g)</td>
<td>28.883</td>
<td>-0.157</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O$_2$ (g)</td>
<td>25.460</td>
<td>1.519</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO (g)</td>
<td>29.322</td>
<td>-0.094</td>
<td>90.3</td>
<td>86.6</td>
</tr>
</tbody>
</table>

Heat capacity: $C_p = a + b X 10^{-2} T$ [J/mole-K], $\Delta H^0$ and $\Delta G^0$ [kJ/mole] are at 298 K and 1 atm.

5. It is proposed to clean tungsten wire (remove trace of the oxide WO$_2$) by heating the wire to 1000 K in a hydrogen atmosphere (1 atm total pressure) in order to take advantage of the following reaction.

$$\text{WO}_2 (s) + 2 \text{H}_2 (g) = \text{W (s)} + 2 \text{H}_2\text{O (g)}$$

Will this work? If so, what is the maximum water impurity level (i.e. partial pressure of water) that can be tolerated in the hydrogen? Free energies of formation are as following,

$$\text{WO}_2(s) : \Delta G^f = - 131600 + 36.6 T \ [\text{cal/mole}] \quad \text{H}_2\text{O (g)} : \Delta G^f = - 58900 + 13.1 T \ [\text{cal/mole}]$$

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

Binary Gibbs-Duhem equation: $x_1 \left( \frac{\partial \bar{\theta}_1}{\partial x_1} \right) + x_2 \left( \frac{\partial \bar{\theta}_2}{\partial x_1} \right) = 0$, $\Delta G^0 = -RT \ln K$

Clausius-Claypeyron Eqn. $\ln p^0 = c - \frac{\Delta h}{RT}$, $\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2}$.

$\Delta H_{rxn}(T) = \Delta H_{rxn}(298 \text{ K}) + \int_{298}^{T} \left[ \sum \nu_i C_{p,i}^0 \right] dT$, Gas constant $R = 1.987 \text{ cal/mole-K}$, or $8.314 \text{ J/mole-K}$