Assigned questions for Lecture 12 are listed below. The questions occur in the following editions of “Physical Chemistry” by P.W. Atkins:

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<tbody>
<tr>
<td></td>
<td>n/a</td>
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<td>3.6</td>
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*Missing from 10th and 11th Eds. (not sure why).

3.6(a) Consider a system consisting of 2.0 mol CO\(_2\)(g), initially at 25°C and 10 atm and confined to a cylinder of cross-section 10.0 cm\(^2\). It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered a perfect gas with \(C_V = 28.8\) J K\(^{-1}\) mol\(^{-1}\) and calculate (a) \(q\), (b) \(w\), (c) \(\Delta U\), (d) \(\Delta T\), (e) \(\Delta S\).

3.6(b) Consider a system consisting of 1.5 mol CO\(_2\)(g), initially at 15°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm\(^2\). The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that carbon dioxide may be considered a perfect gas with \(C_V = 28.8\) J K\(^{-1}\) mol\(^{-1}\), and calculate (a) \(q\), (b) \(w\), (c) \(\Delta U\), (d) \(\Delta T\), (e) \(\Delta S\).

<table>
<thead>
<tr>
<th>Question 12.02</th>
<th>3B.2</th>
<th>3A.11</th>
<th>3.7</th>
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3B.2(a) The enthalpy of vaporization of chloroform (CHCl\(_3\)) is 29.4 kJ mol\(^{-1}\) at its normal boiling point of 334.88 K. Calculate (i) the entropy of vaporization of chloroform at this temperature and (ii) the entropy change of the surroundings.

3B.2(b) The enthalpy of vaporization of methanol is 35.27 kJ mol\(^{-1}\) at its normal boiling point of 64.1 °C. Calculate (i) the entropy of vaporization of methanol at this temperature and (ii) the entropy change of the surroundings.

<table>
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<tr>
<th>Question 12.03</th>
<th>3C.2</th>
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*Same question format, different compounds in the 10th and 11th Eds. vs. earlier editions.*

3.11(a) Calculate the standard Gibbs energy of the reaction 4 HCl(g) + O\(_2\)(g) → 2 Cl\(_2\)(g) + 2 H\(_2\) O(l) at 298 K, from the standard entropies and enthalpies of formation given in the Data section.

3.11(b) Calculate the standard Gibbs energy of the reaction CO(g) + CH\(_3\) OH(l) → CH\(_3\)
COOH(l) at 298 K, from the standard entropies and enthalpies of formation given in the Data section.

3C.2(a) Calculate the standard Gibbs energy of the reaction 4 HI(g) + O$_2$(g) $\rightarrow$ 2 I$_2$(s) + 2 H$_2$O(l) at 298 K, from the standard entropies and enthalpies of formation given in the Resource section.

3C.2(b) Calculate the standard Gibbs energy of the reaction CO(g) + CH$_3$CH$_2$OH(l) $\rightarrow$ CH$_3$CH$_2$COOH(l) at 298 K, from the standard entropies and enthalpies of formation given in the Resource section. The data for CH$_3$CH$_2$COOH(l) are $\Delta_f^o H^o = -510$ kJ mol$^{-1}$, $S^o_m = 191$ J K$^{-1}$ mol$^{-1}$ at 298K.

Question 12.04

<table>
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<tr>
<th>3D.5</th>
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Same question format, different compounds in the 10th and 11th Eds. vs. earlier editions.

9th Ed. and earlier:

3.12(a) The standard enthalpy of combustion of solid phenol (C$_6$H$_5$OH) is -3054 kJ mol$^{-1}$ at 298 K and its standard molar entropy is 144.0 J K$^{-1}$ mol$^{-1}$. Calculate the standard Gibbs energy of formation of phenol at 298 K.

3.12(b) The standard enthalpy of combustion of solid urea (CO(NH$_2$)$_2$) is –632 kJ mol$^{-1}$ at 298 K and its standard molar entropy is 104.60 J K$^{-1}$ mol$^{-1}$. Calculate the standard Gibbs energy of formation of urea at 298 K.

10th and 11th Eds.:

3D.5(a) The standard enthalpy of combustion of ethyl acetate (CH$_3$COOC$_2$H$_5$) is –2231 kJ mol$^{-1}$ at 298 K and its standard molar entropy is 259.4 J K$^{-1}$ mol$^{-1}$. Calculate the standard Gibbs energy of formation of the compound at 298 K.

3D.5(b) The standard enthalpy of combustion of the amino acid glycine (NH$_2$CH$_2$COOH) is –969 kJ mol$^{-1}$ at 298 K and its standard molar entropy is 103.5 J K$^{-1}$ mol$^{-1}$. Calculate the standard Gibbs energy of formation of glycine at 298 K.

Question 12.05

<table>
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<tr>
<th>3A.4</th>
<th>3A.10</th>
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In the 11th Ed., the solutions manual omits the text in grey - I have am not sure why this is the case, except that you do not really need the values of p to do these problems.

3A.4(a) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (i) an isothermal reversible expansion, (ii) an isothermal irreversible expansion against $p_{ex} = 0$, and (iii) an adiabatic reversible expansion.

3A.4(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm$^3$ to 4.60 dm$^3$ in (i) an isothermal reversible expansion, (ii) an isothermal irreversible expansion against $p_{ex} = 0$, and (iii) an adiabatic reversible expansion.
Question 12.06*

**Missing from the 10th and 11th eds. Not sure why.**

**3.5** A Carnot cycle uses 1.00 mol of a monatomic perfect gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (Step 1), and then adiabatically to a temperature of 300 K (Step 2). This expansion is followed by an isothermal compression (Step 3), and then an adiabatic compression (Step 4) back to the initial state. Determine the values of \( q \), \( w \), \( \Delta U \), \( \Delta H \), \( \Delta S \), \( \Delta S_{\text{tot}} \), and \( \Delta G \) for each stage of the cycle and for the cycle as a whole. Express your answer as a table of values.

**Answer 12.01**

**Missing from 10th and 11th Eds. (not sure why).**

\[ E3.6(a) \]

(a) \( q = 0 \) [adiabatic]

(b) \( w = -p_c \Delta V = -(1.01 \times 10^5 \text{ Pa}) \times (20 \text{ cm}) \times (10 \text{ cm}^2) \times \left( \frac{10^{-6} \text{ m}^3}{\text{cm}^3} \right) = -20 \text{ J} \)

(c) \( \Delta U = q + w = 0 - 20 \text{ J} = -20 \text{ J} \)

(d) \( \Delta U = nC_{r,m} \Delta T \) [2.16b]

\[ \Delta T = \frac{-20 \text{ J}}{(2.0 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1})} = -0.347 \text{ K} \]

(e) Entropy is a state function, so we can compute it by any convenient path. Although the specified transformation is adiabatic, a more convenient path is constant-volume cooling followed by isothermal expansion. The entropy change is the sum of the entropy changes of these two steps:

\[
\Delta S = \Delta S_1 + \Delta S_2 = nC_{r,m} \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right) \quad [3.23 \& 3.17]
\]

\[
T_f = T_i - 0.347 \text{ K} = (298.15 \text{ K}) - (0.347 \text{ K}) = 297.803 \text{ K}
\]

\[
V_f = \frac{nRT_f}{p_i} = \frac{(2.0 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm} \text{ K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{10 \text{ atm}} = 4.893 \text{ dm}^3
\]

\[
V_i = V_f + \Delta V = (4.893 + 0.20) \text{ dm}^3 = 5.093 \text{ dm}^3
\]

Substituting these values into the expression for \( \Delta S \) above gives

\[
\Delta S = (2.0 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left( \frac{297.803 \text{ K}}{298.15 \text{ K}} \right)
\]

\[
+ (2.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{5.093 \text{ dm}^3}{4.893 \text{ dm}^3} \right)
\]

\[
= (-0.0671 + 0.666) \text{ J K}^{-1} = +0.60 \text{ J K}^{-1}
\]
\[ E3.6(b) \]

(a) \( q = 0 \) [adiabatic]

(b) \[ w = -p\Delta V = -(1.5 \text{ atm}) \times \left( 1.01 \times 10^3 \text{ Pa atm}^{-1} \right) \times (100.0 \text{ cm}^2) \times (15 \text{ cm}) \times \left( \frac{1 \text{ m}^3}{10^5 \text{ cm}^3} \right) \]

\[ = -227.2 \text{ J} = -230 \text{ J} \]

(c) \[ \Delta U = q + w = 0 - 230 \text{ J} = -230 \text{ J} \]

(d) \[ \Delta U = nC_v \Delta T \]

\[ \Delta T = \frac{\Delta U}{nC_v} = \frac{-227.2 \text{ J}}{(1.5 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1})} = -5.3 \text{ K} \]

(e) Entropy is a state function, so we can compute it by any convenient path. Although the specified transformation is adiabatic, a more convenient path is constant-volume cooling followed by isothermal expansion. The entropy change is the sum of the entropy changes of these two steps:

\[ \Delta S = \Delta S_1 + \Delta S_2 = nC_v \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right) \]

\[ T_f = 288.15 \text{ K} - 5.26 \text{ K} = 282.9 \text{ K} \]

\[ V_i = \frac{nRT}{p_i} = \frac{(1.5 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm}^{-1} \text{ K}^{-1} \text{ mol}^{-1}) \times (288.2 \text{ K})}{9.0 \text{ atm}} \]

\[ = 3.942 \text{ dm}^3 \]

\[ V_f = 3.942 \text{ dm}^3 + (100 \text{ cm}^2) \times (15 \text{ cm}) \times \left( \frac{1 \text{ dm}^3}{1000 \text{ cm}^2} \right) \]

\[ = 3.942 \text{ dm}^3 + 1.5 \text{ dm}^3 = 5.44 \text{ dm}^3 \]

\[ \Delta S = (1.5 \text{ mol}) \times \left( 28.8 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \left( \frac{282.9}{288.2} \right) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{5.44}{3.942} \right) \]

\[ = 1.5 \text{ mol}(-0.5346 \text{ J K}^{-1} \text{ mol}^{-1} + 2.678 \text{ J K}^{-1} \text{ mol}^{-1}) = 3.2 \text{ J K}^{-1} \]
Answer 12.06

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**Missing from the 10th and 11th eds. Not sure why.**

### Step 1

\[
\Delta U = \Delta H = 0 \quad \text{[isothermal]}
\]

\[
w = -nRT \ln \left( \frac{V_f}{V_i} \right) = nRT \ln \left( \frac{P_i}{P_f} \right) \quad [2.10, \text{and Boyle's law}]
\]

\[
= (1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K}) \times \ln \left( \frac{1.00 \text{ atm}}{10.0 \text{ atm}} \right) = -11.5 \text{ kJ}
\]

\[
q = -w = 11.5 \text{ kJ}
\]

\[
\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) [3.17] = -nR \ln \left( \frac{P_i}{P_f} \right) \quad [\text{Boyle's law}]
\]

\[
= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left( \frac{1.00 \text{ atm}}{10.0 \text{ atm}} \right) = +19.1 \text{ J K}^{-1}
\]

\[
\Delta S_{\text{sur}} = -\Delta S_{\text{system}} \quad \text{[reversible process]} = -19.1 \text{ J K}^{-1}
\]

\[
\Delta S_{\text{tot}} = \Delta S_{\text{system}} + \Delta S_{\text{sur}} = 0
\]

\[
\Delta G = \Delta H - T \Delta S = 0 - (600 \text{ K}) \times (19.1 \text{ J K}^{-1}) = -11.5 \text{ kJ mol}^{-1}
\]

### Step 2

\[
q = 0 \quad \text{[adiabatic]}
\]

\[
\Delta U = nC_{V,m} \Delta T \quad [2.16b]
\]

\[
= (1.00 \text{ mol}) \times (\frac{1}{2}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K} - 600 \text{ K}) = -3.74 \text{ kJ}
\]

\[
w = \Delta U = -3.74 \text{ kJ}
\]

(continued next page)
\[
\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T = (-3.74 \text{ kJ}) + (1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-300 \text{ K}) = \boxed{-6.23 \text{ kJ}}
\]

\[
\Delta S = \Delta S(\text{sur}) = 0 \quad \text{[reversible adiabatic process]}
\]

\[
\Delta S_{\text{tot}} = 0
\]

\[
\Delta G = \Delta(H - TS) = \Delta H - S\Delta T \quad \text{[no change in entropy]}
\]

Although the change in entropy is known to be zero, the entropy itself is not known, so \(\Delta S\) is indeterminate.

**Step 3**

These quantities may be calculated in the same manner as for Step 1 or more easily as follows:

\[
\Delta U = \Delta H = 0 \quad \text{[isothermal]}
\]

\[
\eta_{\text{rev}} = 1 - \frac{T_c}{T_h} = [3.10] = 1 - \frac{300 \text{ K}}{600 \text{ K}} = 0.500 = 1 + \frac{q_c}{q_h} = [3.9]
\]

\[
q_c = -0.500q_h = -(0.500) \times (11.5 \text{ kJ}) = -5.74 \text{ kJ}
\]

\[
q_c = \boxed{-5.74 \text{ kJ}} \quad w = -q_c = \boxed{5.74 \text{ kJ}}
\]

\[
\Delta S = \frac{q_{\text{rev}}}{T} = \frac{5.74 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{-19.1 \text{ J K}^{-1}}
\]

\[
\Delta S(\text{sur}) = -\Delta S(\text{system}) = +19.1 \text{ J K}^{-1}
\]

\[
\Delta S_{\text{tot}} = 0
\]

\[
\Delta G = \Delta H - T\Delta S = 0 - (300 \text{ K}) \times (-19.1 \text{ J K}^{-1}) = \boxed{+5.73 \text{ kJ}}
\]

**Step 4**

\(\Delta U\) and \(\Delta H\) are the negative of their values in Step 2. (Initial and final temperatures reversed.)

\[
\Delta U = \boxed{+3.74 \text{ kJ}} \quad \Delta H = \boxed{+6.23 \text{ kJ}} \quad q = 0 \quad \text{[adiabatic]}
\]

\[
w = \Delta U = \boxed{+3.74 \text{ kJ}}
\]

\[
\Delta S = \Delta S(\text{sur}) = 0 \quad \text{[reversible adiabatic process]}
\]

\[
\Delta S_{\text{tot}} = 0
\]

Again \(\Delta G = \Delta(H - TS) = \Delta H - S\Delta T\) [no change in entropy]

but \(S\) is not known, so \(\Delta G\) is indeterminate.

**Cycle**

\[
\Delta U = \Delta H = \Delta S = \Delta G = 0 \quad \text{[\(\Delta\) (state function) = 0 for any cycle]}
\]

\[
\Delta S(\text{sur}) = 0 \quad \text{[all reversible processes]}
\]

\[
\Delta S_{\text{tot}} = 0
\]

\[
q(\text{cycle}) = (11.5 - 5.74) \text{ kJ} = \boxed{5.8 \text{ kJ}} \quad w(\text{cycle}) = -q(\text{cycle}) = \boxed{-5.8 \text{ kJ}}
\]