

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

10th edition	9th edition	8th edition
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**Note:** The letter “P” in front of a number indicates that the question is in the “Problem” category as opposed to the “Exercise” category in Atkins’ books. Updates are highlighted in yellow. There are a fair number of differences and missing questions, and unfortunately, a lot of good problems were removed years ago from earlier editions.

### Question 12.01\*

n/a	3.6	3.6
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*Missing from 10th Ed. (not sure why).*

**3.6(a)** Consider a system consisting of 2.0 mol CO<sub>2</sub>(g), initially at 25°C and 10 atm and confined to a cylinder of cross-section 10.0 cm<sup>2</sup>. 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  $C_{v,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$  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<sub>2</sub>(g), initially at 15°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm<sup>2</sup>. 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  $C_{v,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$ , and calculate (a)  $q$ , (b)  $w$ , (c)  $\Delta U$ , (d)  $\Delta T$ , (e)  $\Delta S$ .

### Question 12.02

3A.11	3.7	3.7
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**3A.11(a)** The enthalpy of vaporization of chloroform (CHCl<sub>3</sub>) is 29.4 kJ mol<sup>-1</sup> 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.

**3A.11(b)** The enthalpy of vaporization of methanol is 35.27 kJ mol<sup>-1</sup> 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.

### Question 12.03

3C.2	3.11	3.11
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*Same question format, different compounds in the 10th ed. vs. earlier editions.*

**3.11(a)** Calculate the standard Gibbs energy of the reaction  $4 \text{ HCl(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{ Cl}_2\text{(g)} + 2 \text{ H}_2\text{O(l)}$  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  $\text{CO(g)} + \text{CH}_3\text{OH(l)} \rightarrow \text{CH}_3$

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  $4 \text{HI(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{I}_2\text{(s)} + 2 \text{H}_2\text{O(l)}$  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  $\text{CO(g)} + \text{CH}_3\text{CH}_2\text{OH(l)} \rightarrow \text{CH}_3\text{CH}_2\text{COOH(l)}$  at 298 K, from the standard entropies and enthalpies of formation given in the *Resource section*.

### Question 12.04

3C.5	3.12	3.12
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*Same question format, different compounds in the 10th ed. vs. earlier editions.*

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

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

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

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

### Question 12.05

3A.10	3.13	3.13
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**3A.10(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  $p_{\text{ex}} = 0$ , and (iii) an adiabatic reversible expansion.

**3A.10(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  $1.20 \text{ dm}^3$  to  $4.60 \text{ dm}^3$  in (i) an isothermal reversible expansion, (ii) an isothermal irreversible expansion against  $p_{\text{ex}} = 0$ , and (iii) an adiabatic reversible expansion.

**Question 12.06\***

n/a	P3.5	P3.5
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Missing from the 10th ed. 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**

n/a	3.6	3.6
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Missing from 10th Ed. (not sure why).

**E3.6(a)** (a)  $q = \boxed{0}$  [adiabatic]

(b)  $w = -p_{\text{ex}}\Delta V$  [2.8]  $= -(1.01 \times 10^5 \text{ Pa}) \times (20 \text{ cm}) \times (10 \text{ cm}^2) \times \left(\frac{10^{-6} \text{ m}^3}{\text{cm}^3}\right) = -20 \text{ J}$

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

(d)  $\Delta U = nC_{V,m}\Delta T$  [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:

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

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

$$V_i = \frac{nRT}{p_i} = \frac{(2.0 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{10 \text{ atm}} = 4.893 \text{ dm}^3$$

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

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

$$\begin{aligned} \Delta S &= (2.0 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{297.803 \text{ K}}{298.15 \text{ K}}\right) \\ &\quad + (2.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{5.093 \text{ dm}^3}{4.893 \text{ dm}^3}\right) \\ &= (-0.0671 + 0.666) \text{ J K}^{-1} = \boxed{+0.60 \text{ J K}^{-1}} \end{aligned}$$

**E3.6(b)** (a)  $q = 0$  [adiabatic]

$$(b) \quad w = -p_{\text{ext}}\Delta V = -(1.5 \text{ atm}) \times \left( \frac{1.01 \times 10^5 \text{ Pa}}{\text{atm}} \right) \times (100.0 \text{ cm}^2) \times (15 \text{ cm}) \times \left( \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \\ = -227.2 \text{ J} = \boxed{-230 \text{ J}}$$

$$(c) \quad \Delta U = q + w = 0 - 230 \text{ J} = \boxed{-230 \text{ J}}$$

$$(d) \quad \Delta U = nC_{V,m}\Delta T$$

$$\Delta T = \frac{\Delta U}{nC_{V,m}} = \frac{-227.2 \text{ J}}{(1.5 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{-5.3 \text{ K}}$$

(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:

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

$$T_f = 288.15 \text{ K} - 5.26 \text{ K} = 282.9 \text{ K}$$

$$V_i = \frac{nRT}{p_i} = \frac{(1.5 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (288.2 \text{ K})}{9.0 \text{ atm}} \\ = 3.942 \text{ dm}^3$$

$$V_f = 3.942 \text{ dm}^3 + (100 \text{ cm}^2) \times (15 \text{ cm}) \times \left( \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \right) \\ = 3.942 \text{ dm}^3 + 1.5 \text{ dm}^3 = 5.44 \text{ dm}^3$$

$$\Delta S = (1.5 \text{ mol}) \times \left\{ (28.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left( \frac{282.9}{288.2} \right) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left( \frac{5.44}{3.942} \right) \right\} \\ = 1.5 \text{ mol}(-0.5346 \text{ J K}^{-1} \text{ mol}^{-1} + 2.678 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{3.2 \text{ J K}^{-1}}$$

## Answer 12.06

n/a	P3.5	P3.5
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Missing from the 10th ed. Not sure why.

P3.5	Step 1	Step 2	Step 3	Step 4	Cycle
$q$	+11.5 kJ	0	-5.74 kJ	0	-5.8 kJ
$w$	-11.5 kJ	-3.74 kJ	+5.74 kJ	+3.74 kJ	-5.8 kJ
$\Delta U$	0	-3.74 kJ	0	+3.74 kJ	0
$\Delta H$	0	-6.23 kJ	0	+6.23 kJ	0
$\Delta S$	+19.1 J K <sup>-1</sup>	0	-19.1 J K <sup>-1</sup>	0	0
$\Delta S_{\text{tot}}$	0	0	0	0	0
$\Delta G$	-11.5 kJ	?	+5.73 kJ	?	0

Step 1

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

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

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

$$q = -w = \boxed{11.5 \text{ kJ}}$$

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

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

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

$$\Delta S_{\text{tot}} = \Delta S(\text{system}) + \Delta S(\text{sur}) = \boxed{0}$$

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

Step 2

$$q = \boxed{0} \text{ [adiabatic]}$$

$$\Delta U = nC_{v,m}\Delta T \text{ [2.16b]}$$

$$= (1.00 \text{ mol}) \times \left(\frac{3}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K} - 600 \text{ K}) = \boxed{-3.74 \text{ kJ}}$$

$$w = \Delta U = \boxed{-3.74 \text{ kJ}}$$

(continued next page)

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$

$$= (-3.74 \text{ kJ}) + (1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-300 \text{ K}) = \boxed{-6.23 \text{ kJ}}$$

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

$$\Delta S_{\text{tot}} = \boxed{0}$$

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

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

*Step 3*

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

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

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

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

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

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

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

$$\Delta S_{\text{tot}} = \boxed{0}$$

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

*Step 4*

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

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

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

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

$$\Delta S_{\text{tot}} = \boxed{0}$$

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*

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

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

$$\Delta S_{\text{tot}} = \boxed{0}$$

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

**Instructor version answers for the 9<sup>th</sup> edition (see above for 8<sup>th</sup>/10<sup>th</sup> editions numbers):**

**3.6 (a)**  $q = 0$ , (b)  $w = -20 \text{ J}$ , (c)  $\Delta U = -20 \text{ J}$ , (d)  $\Delta T = -0.347 \text{ K}$  (e)  $+0.60 \text{ J K}^{-1}$

**3.7 (a)**  $\Delta_{\text{vap}}S = +87.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ; (b) if reversible,  $\Delta S_{\text{tot}} = 0$ ,  $\Delta S_{\text{surr}} = -87.8 \text{ J K}^{-1} \text{ mol}^{-1}$

**3.11**  $\Delta_r H = -202.42 \text{ kJ mol}^{-1}$ ;  $\Delta_r S = -366.82 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $\Delta_r G = -93.05 \text{ kJ mol}^{-1}$

**3.12**  $\Delta_r G = -50 \text{ kJ mol}^{-1}$

**3.13**

	$\Delta S (\text{gas}) (\text{J K}^{-1})$	$\Delta S_{\text{surr}} (\text{J K}^{-1})$	$\Delta S_{\text{tot}} (\text{J K}^{-1})$
(a)	+2.9	-2.9	0
(b)	+2.9	0	+2.9
(c)	0	0	0

**P3.5** (*see student solution manual or above*)