

Assigned questions for Lecture 11 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 11.01

n/a	n/a	n/a
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Missing from 8th and later editions (not sure why).

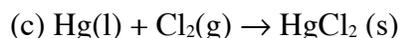
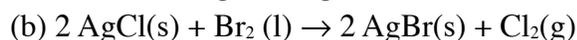
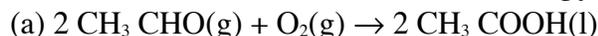
Ex. 4.14a, 7th edition. Calculate the change in entropy when 50 g of water at 80 °C is poured into 100 g of water at 10 °C in an insulated vessel given that $C_{p,m} = 75.5 \text{ J K}^{-1} \text{ mol}^{-1}$.

Ex. 4.14b, 7th edition. Calculate the change in entropy when 25 g of ethanol at 50 °C is poured into 70 g of ethanol at 10 °C in an insulated vessel given that $C_{p,m} = 111.5 \text{ J K}^{-1} \text{ mol}^{-1}$.

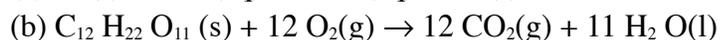
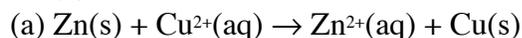
Question 11.02

3B.2	3.8	3.8
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3.8(a) Calculate the standard reaction entropy at 298 K of



3.8(b) Calculate the standard reaction entropy at 298 K of



Question 11.03

3C.1	3.9	3.9
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3.9(a) Combine the reaction entropies calculated in Exercise 3.8a (3B.2a, 10th Ed) with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

3.9(b) Combine the reaction entropies calculated in Exercise 3.8b (3B.2b, 10th Ed) with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

Question 11.04

3C.4	3.10	3.10
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3.10(a) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8a (3B.2a, 10th Ed).

3.10(b) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8b (3B.2b, 10th Ed).

Question 11.05

n/a	n/a	n/a
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Missing from 8th and later editions (not sure why).

Ex. 4.24a, 7th edition. Calculate the change in entropy when a monatomic perfect gas is compressed to half of its initial volume and simultaneously heated to twice its initial temperature.

Ex. 4.24b, 7th edition. Calculate the change in entropy when a diatomic perfect gas is compressed to one-third of its initial volume and simultaneously heated to three times its initial temperature.

Question 11.06

3C.3	3.14	3.14
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3C.3(a) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

3C.3(b) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

Question 11.07

n/a	3.15	3.15
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Missing from 10th Ed.

3.15(a) (a) Calculate the Carnot efficiency of a primitive steam engine operating on steam at 100°C and discharging at 60°C. (b) Repeat the calculation for a modern steam turbine that operates with steam at 300°C and discharges at 80°C.

3.15(b) A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

Answer 11.01

n/a	n/a	n/a
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Missing from 8th and later editions (not sure why).

E4.14(a) Find the common final temperature T_f by noting that the heat lost by the hot sample is gained by the cold sample

$$-n_1 C_{p,m}(T_f - T_{i1}) = n_2 C_{p,m}(T_f - T_{i2})$$

Hence, $T_f = \frac{n_1 T_{i1} + n_2 T_{i2}}{n_1 + n_2}$

Since $\frac{n_1}{n_2} = \frac{1}{2}$, $T_f = \frac{1}{3}(353 \text{ K} + 2 \times 283 \text{ K}) = 306 \text{ K}$

The total change in entropy is that of the 50 g sample (ΔS_1) plus that of the 100 g sample (ΔS_2).

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = n_1 C_{p,m} \ln \frac{T_f}{T_{i1}} + n_2 C_{p,m} \ln \frac{T_f}{T_{i2}} \quad [\text{constant pressure, 4.20}] \\ &= \left(\frac{50 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (75.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\ln \frac{306}{353} + 2 \ln \frac{306}{283} \right) = \boxed{+2.8 \text{ J K}^{-1}} \end{aligned}$$

E4.14(b) Find the final temperature by equating the heat lost by the hot sample to the heat gained by the cold sample.

$$-n_1 C_{p,m}(T_f - T_{i1}) = n_2 C_{p,m}(T_f - T_{i2})$$

$$T_f = \frac{n_1 T_{i1} + n_2 T_{i2}}{n_1 + n_2} = \frac{\frac{1}{M}(m_1 T_{i1} + m_2 T_{i2})}{\frac{1}{M}(m_1 + m_2)}$$

$$= \frac{m_1 T_{i1} + m_2 T_{i2}}{m_1 + m_2}$$

$$= \frac{(25 \text{ g}) \times (323 \text{ K}) + (70 \text{ g}) \times (293 \text{ K})}{25 \text{ g} + 70 \text{ g}} = 300.9 \text{ K}$$

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = n_1 C_{p,m} \ln \left(\frac{T_f}{T_{i1}} \right) + n_2 C_{p,m} \ln \left(\frac{T_f}{T_{i2}} \right) \\ &= \left\{ \left(\frac{25 \text{ g}}{46.07 \text{ g mol}^{-1}} \right) \ln \left(\frac{300.9}{323} \right) + \left(\frac{70 \text{ g}}{46.07 \text{ g mol}^{-1}} \right) \times \ln \left(\frac{300.9}{293} \right) \right\} C_{p,m} \\ &= \left\{ -3.846 \times 10^{-2} + 4.043 \times 10^{-2} \right\} C_{p,m} \\ &= (0.196 \times 10^{-2} \text{ mol}) \times (111.5 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{0.2 \text{ J K}^{-1}} \end{aligned}$$

Answer 11.05

n/a	n/a	n/a
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Missing from 8th and later editions (not sure why).

A-list:

- E4.24** The same final state is attained if the change takes place in two stages, one being isothermal compression

$$\Delta S_1 = nR \ln \frac{V_f}{V_i} [4.17] = nR \ln \frac{1}{2} = -nR \ln 2$$

and the second, heating at constant volume

$$\Delta S_2 = nC_{V,m} \ln \frac{T_f}{T_i} [4.20] = nC_{V,m} \ln 2$$

The overall entropy change is therefore

$$\Delta S = -nR \ln 2 + nC_{V,m} \ln 2 = \boxed{n(C_{V,m} - R) \ln 2}$$

- E4.24(b)** Because entropy is a state function, we can choose any convenient path between the initial and final states.

Choose isothermal compression followed by constant-volume heating

$$\begin{aligned} \Delta S &= nR \ln \left(\frac{V_f}{V_i} \right) + nC_{V,m} \ln \left(\frac{T_f}{T_i} \right) \\ &= -nR \ln 3 + nC_{V,m} \ln 3 \\ &= n(C_{V,m} - R) \ln 3 \quad C_{V,m} = \frac{5}{2}R \text{ for a diatomic perfect gas} \end{aligned}$$

$$\boxed{\Delta S = \frac{3}{2}nR \ln 3}$$

Answer 11.07

n/a	3.15	3.15
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Missing from 10th Ed.

$$\text{E3.15(a)} \quad \eta_{\text{rev}} = 1 - \frac{T_c}{T_h} \quad [3.10]$$

$$\eta = 1 - \frac{333 \text{ K}}{373 \text{ K}} = \boxed{0.11} \quad (11\% \text{ efficiency for the old steam engine})$$

$$\eta = 1 - \frac{353 \text{ K}}{573 \text{ K}} = \boxed{0.38} \quad (38\% \text{ efficiency for the modern turbine})$$

$$\text{E3.15(b)} \quad (\text{a}) \quad \varepsilon = 1 - \frac{T_c}{T_h} \quad [3.10] = 1 - \frac{500 \text{ K}}{1000 \text{ K}} = \boxed{0.500}$$

$$(\text{b}) \quad \text{Maximum work} = \varepsilon |q_h| = (0.500) \times (1.0 \text{ kJ}) = \boxed{0.50 \text{ kJ}}$$

$$(\text{c}) \quad \varepsilon_{\text{max}} = \varepsilon_{\text{rev}} \quad \text{and} \quad |w_{\text{max}}| = |q_h| - |q_{c,\text{min}}|$$

$$\begin{aligned} |q_{c,\text{min}}| &= |q_h| - |w_{\text{max}}| \\ &= 1.0 \text{ kJ} - 0.50 \text{ kJ} \\ &= \boxed{0.5 \text{ kJ}} \end{aligned}$$

Answers:

Ex. 4.14a, 7th edition

$$+2.8 \text{ J K}^{-1}$$

Ex. 4.14b, 7th edition

$$0.2 \text{ J K}^{-1}$$

Ex. 4.24a, 7th edition

$$n(C_{V,m} - R) \ln 2$$

Ex. 4.24b, 7th edition

$$(3/2)nR \ln 3$$

A-list answers for the 9th edition:

3.5 93.4 J K^{-1}

3.8 $-386.1 \text{ J K}^{-1} \text{ mol}^{-1}; +92.6 \text{ J K}^{-1} \text{ mol}^{-1}; -153.1 \text{ J K}^{-1} \text{ mol}^{-1}$

3.9 $-521.5 \text{ kJ mol}^{-1}; +25.8 \text{ kJ mol}^{-1}; -178.7 \text{ kJ mol}^{-1}$

3.10 $-522.1 \text{ kJ mol}^{-1}; +25.78 \text{ kJ mol}^{-1}; -178.6 \text{ kJ mol}^{-1}$

3.14 $817.90 \text{ kJ mol}^{-1}$

3.15 $\epsilon = 0.11; \epsilon = 0.38$