Assigned questions for Lecture 10 are listed below (there are two sets). The questions occur in the following editions of "Physical Chemistry" by P.W. Atkins:

10th edition	9th edition	8th edition

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. <mark>Updates are highlighted in yellow.</mark> *There are a fair number of differences and missing questions, and unfortunately, a lot of good problems were removed years ago from earlier editions.*

Set 1

Question 10.01

3A.3	3.1	3.1

Slight variation: 10th vs. 8th and 9th Eds.

3.1(a) Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at (a) 0°C, (b) 100°C.
3.1(b) Calculate the change in entropy when 50 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (a) 0°C, (b) 70°C.

3A.3(a) Calculate the change in entropy when 100 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (i) 0 °C, (ii) 50 °C.
3A.3(b) Calculate the change in entropy when 250 kJ of energy is transferred reversibly and isothermally as heat to a large block of lead at (i) 20 °C, (ii) 100 °C.

Question 10.02

3A.7	3.2	3.2

3.2(a) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is 146.22 J K^{-1} mol^{-1} at 298 K.
3.2(b) Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is 154.84 J K^{-1} mol^{-1} at 298 K.

Question 10.03

3A.8	3.3	3.3

3.3(a) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,m} = (5/2)R$, is changed from 25°C and 1.00 atm to 125°C and 5.00 atm. How do you rationalize the sign of ΔS?
3.3(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = (7/2)R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS?

Question 10.04

n/a	3.4	3.4

Question is missing from 10th Ed.

3.4(a) A sample consisting of 3.00 mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,m} = 27.5$ J K^{-1} mol^{-1}, calculate q, w, ΔU, ΔH, and ΔS.
3.4(b) A sample consisting of 2.00 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{V,m} = 27.5$ J K^{-1} mol^{-1}, calculate q, w, ΔU, ΔH, and ΔS.

Set 2

Question 10.05

3A.9	3.5	3.5

Slight variations: 10th vs. 8th and 9th Eds.

3.5(a) Calculate ΔH and ΔS_{tot} when two copper blocks, each of mass 10.0 kg, one at 100°C and the other at 0°C, are placed in contact in an isolated container. The specific heat capacity of copper is 0.385 J K^{-1} g^{-1} and may be assumed constant over the temperature range involved.
3.5(b) Calculate ΔH and ΔS_{tot} when two iron blocks, each of mass 1.00 kg, one at 200°C and the other at 25°C, are placed in contact in an isolated container. The specific heat capacity of iron is 0.449 J K^{-1} g^{-1} and may be assumed constant over the temperature range involved.

3A.9(a) Calculate ΔS_{tot} when two copper blocks, each of mass 1.00 kg, one at 50 °C and the other at 0 °C are placed in contact in an isolated container. The specific heat capacity of copper is 0.385 J K^{-1} g^{-1} and may be assumed constant over the temperature range involved.
3A.9(b) Calculate ΔS_{tot} when two iron blocks, each of mass 10.0 kg, one at 100 °C and the other at 25 °C, are placed in contact in an isolated container. The specific heat capacity of iron is 0.449 J K^{-1} g^{-1} and may be assumed constant over the temperature range involved.

Question 10.06

n/a	n/a	n/a

Missing from 8th and later editions (not sure why).
Ex. 4.9a, 7th edition. Calculate the increase in entropy when 1.00 mol of a monatomic perfect gas with $C_{p,m} = (5/2)R$ is heated from 300 K to 600 K and simultaneously expanded from 30.0 L to 50.0 L.
Ex. 4.9b, 7th edition. Calculate the increase in entropy when 3.50 mol of a monatomic perfect gas with $C_{p,m} = (5/2)R$ is heated from 250 K to 700 K and simultaneously expanded from 20.0 L to 60.0 L.

Question 10.07

n/a	n/a	n/a

Missing from 8th and later editions (not sure why).
Ex. 4.10a, 7th edition. A system undergoes a process in which the entropy change is +2.41 J K^{-1}. During the process, 1.00 kJ of heat is added to the system at 500 K. Is the process thermodynamically reversible? Explain your reasoning.
Ex. 4.10b, 7th edition. A system undergoes a process in which the entropy change is +5.51 J K^{-1}. During the process,1.50 kJ of heat is added to the system at 350 K. Is the process thermodynamically reversible? Explain your reasoning.

Question 10.08

n/a	n/a	n/a

Missing from 8th and later editions (not sure why).
Ex. 4.11a, 7th edition. A sample of aluminum of mass 1.75 kg is cooled at constant pressure from 300 K to 265 K. Calculate (a) the energy that must be removed as heat and (b) the change in the entropy of the sample.
Ex. 4.11b, 7th edition. A sample of copper of mass 2.75 kg is cooled at constant pressure from 330 K to 275 K. Calculate (a) the energy that must be removed as heat and (b) the change in the entropy of the sample.

Question 10.09

n/a	n/a	n/a

Missing from 8th and later editions (not sure why).
Ex. 4.12a, 7th edition. A sample of methane gas of mass 25 g at 250 K and 18.5 atm expands isothermally until the pressure is 2.5 atm. Calculate the change in entropy of the gas.
Ex. 4.12b, 7th edition. A sample of nitrogen gas of mass 35 g at 230 K and 21.1 atm expands isothermally until the pressure is 4.3 atm. Calculate the change in entropy of the gas.

Question 10.10

n/a	n/a	n/a

Ex. 4.13a, 7th edition. A sample of perfect gas that initially occupies 15.0 L at 250 K and 1.00 atm is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by 5.0 J K^{-1}?
Ex. 4.13b, 7th edition. A sample of perfect gas that initially occupies 11.0 L at 270 K and 1.20 atm is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by 3.0 J K^{-1}?

Answer 10.04

n/a	3.4	3.4

Question is missing from 10th Ed.

E3.4(a) For an adiabatic reversible process, $q = q_{rev} = \boxed{0}$.

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \boxed{0}$$

$\Delta U = nC_{V,m}\Delta T \,[2.16b] = (3.00 \text{ mol}) \times (27.5 \text{ J K}^{-1}\text{mol}^{-1}) \times (50 \text{ K}) = 4.1 \times 10^3 \text{ J}$
$\quad = \boxed{+4.1 \text{ kJ}}$

$w = \Delta U$ [first law with $q = 0$]

$\Delta H = nC_{p,m}\Delta T \,[2.23b]$

$C_{p,m} = C_{V,m} + R \,[2.26] = (27.5 + 8.3) \text{ J K}^{-1}\text{mol}^{-1} = 35.8 \text{ J K}^{-1}\text{mol}^{-1}$

$\Delta H = (3.00 \text{ mol}) \times (35.8 \text{ J K}^{-1}\text{mol}^{-1}) \times (50 \text{ K}) = 5.4 \times 10^3 \text{ J} = \boxed{+5.4 \text{ kJ}}$

COMMENT. Neither initial nor final pressures and volumes are needed for the solution to this exercise.

E3.4(b) $q = q_{rev} = 0$ [adiabatic reversible process]

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \boxed{0}$$

$\Delta U = nC_{V,m}\Delta T = (2.00 \text{ mol}) \times (27.5 \text{ J K}^{-1}\text{mol}^{-1}) \times (300 - 250) \text{ K}$
$\quad\quad\quad\quad = 2750 \text{ J} = \boxed{+2.75 \text{ kJ}}$

$w = \Delta U - q = 2.75 \text{ kJ} - 0 = \boxed{2.75 \text{ kJ}}$

$\Delta H = nC_{p,m}\Delta T$

$C_{p,m} = C_{V,m} + R = (27.5 \text{ J K}^{-1}\text{mol}^{-1} + 8.314 \text{ J K}^{-1}\text{mol}^{-1}) = 35.81\overline{4} \text{ J K}^{-1}\text{mol}^{-1}$

So $\Delta H = (2.00 \text{ mol}) \times (35.81\overline{4} \text{ J K}^{-1}\text{mol}^{-1}) \times (+50 \text{ K}) = 358\overline{1.4} \text{ J} = \boxed{3.58 \text{ kJ}}$

Answer 10.06

n/a	n/a	n/a

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

E4.9(a)

$$\Delta S = nC_{V,m} \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) \quad \text{[Example 4.3]}$$

$$C_{V,m} = C_{p,m} - R = \tfrac{5}{2}R - R = \tfrac{3}{2}R$$

$$\Delta S = (1.00\,\text{mol}) \times \left(\frac{3}{2}\right) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \ln\left(\frac{600\,\text{K}}{300\,\text{K}}\right)$$

$$+ (1.00\,\text{mol}) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{50.0\,\text{L}}{30.0\,\text{L}}\right) = \boxed{+12.9\,\text{J K}^{-1}}$$

E4.9(b) However the change occurred, ΔS has the same value as if the change happened by reversible heating at constant volume (step 1) followed by reversible isothermal expansion (step 2)

$$\Delta S = \Delta S_1 + \Delta S_2$$

For the first step

$$\Delta S_1 = \int \frac{dq_{rev}}{T} = \int \frac{C_{V,m}\,dT}{T} = C_{V,m} \ln\frac{T_f}{T_i} \quad [C_{V,m} = C_{p,m} - R]$$

$$= (3.50\,\text{mol}) \times \left(\frac{3}{2}\right) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\frac{700\,\text{K}}{250\,\text{K}} = 44.9\,\text{J K}^{-1}$$

and for the second

$$\Delta S_2 = \int \frac{dq_{rev}}{T} = \frac{q_{rev}}{T}$$

where $q_{rev} = -w = \int p\,dV = nRT \ln\frac{V_f}{V_i}$,

so $\Delta S_2 = nR \ln\frac{p_i}{p_f} = (3.50\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\frac{60.0\,\text{L}}{20.0\,\text{L}} = 32.0\,\text{J K}^{-1}$

$$\Delta S = 44.9 + 32.0\,\text{J K}^{-1} = \boxed{76.9\,\text{J K}^{-1}}$$

Answer 10.07

n/a	n/a	n/a

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

E4.10(a) $\Delta S = \dfrac{q_{rev}}{T}$ [constant temperature]

If reversible $q = q_{rev}$.

$$q_{rev} = T\Delta S = (500\,\text{K}) \times (2.41\,\text{J K}^{-1}) = 1.21\,\text{kJ}$$

$$1.21\,\text{kJ} \neq 1.00\,\text{kJ} = q$$

Therefore, the process is | not reversible. |

E4.10(b) $\Delta S = \dfrac{q_{rev}}{T}$ If reversible $q = q_{rev}$

$$q_{rev} = T\Delta S = (5.51\,\text{J K}^{-1}) \times (350\,\text{K})$$
$$= 192\overline{8}.5\,\text{J}$$
$$q = 1.50\,\text{kJ} \neq 19.3\,\text{kJ} = q_{rev}$$

$q \neq q_{rev}$; therefore the process is | not reversible |

Answer 10.08

n/a	n/a	n/a

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

E4.11(a) (a) $\Delta H = \int_{T_1}^{T_2} n C_{p,\text{m}} \, dT$ [constant pressure]

$C_{p,\text{m}}/(\text{J K}^{-1}\,\text{mol}^{-1}) = (a + bT)$ [Table 2.2], $a = 20.67$, $b = 12.38 \times 10^{-3}\,\text{K}^{-1}$

$\Delta H = \int_{T_1}^{T_2} n(a + bT)\,\text{J K}^{-1}\,\text{mol}^{-1}\,dT$

$= na(T_2 - T_1)\,\text{J K}^{-1}\,\text{mol}^{-1} + \frac{1}{2}nb(T_2^2 - T_1^2)\,\text{J K}^{-1}\,\text{mol}^{-1}$

$n = \dfrac{1.75 \times 10^3\,\text{g}}{26.98\,\text{g mol}^{-1}} = 64.8\bar{6}\,\text{mol}$

$\Delta H = \big[(64.8\bar{6}\,\text{mol}) \times (20.67) \times (265 - 300)\,\text{K}$

$+ \left(\tfrac{1}{2}\right) \times (64.8\bar{6}\,\text{mol}) \times (12.38 \times 10^{-3}\,\text{K}^{-1}) \times (265^2 - 300^2)\,\text{K}^2\big]\,\text{J K}^{-1}\,\text{mol}^{-1}$

$\Delta H = -54.9 \times 10^3\,\text{J} = \boxed{-54.9\,\text{kJ}}$

E4.11(b) (a) The heat flow is

$q = C_p \Delta T = n C_{p,\text{m}} \Delta T$

$= \left(\dfrac{2.75\,\text{kg}}{63.54 \times 10^{-3}\,\text{kg mol}^{-1}}\right) \times (24.44\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (275 - 330)\,\text{K}$

$= \boxed{-58.2 \times 10^3\,\text{J}}$

(b) $\Delta S = \int \dfrac{dq_{\text{rev}}}{T} = \int \dfrac{C_p\,dT}{T} = n C_{p,\text{m}} \ln \dfrac{T_\text{f}}{T_\text{i}}$

$= \left(\dfrac{2.75\,\text{kg}}{63.54 \times 10^{-3}\,\text{kg mol}^{-1}}\right) \times (24.44\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln \dfrac{275\,\text{K}}{330\,\text{K}} = \boxed{-193\,\text{J K}^{-1}}$

Answer 10.09

n/a	n/a	n/a

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

E4.12(a)

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) \text{ [4.17]}; \qquad \frac{p_i}{p_f} = \frac{V_f}{V_i} \text{ [Boyle's law]}$$

$$\Delta S = nR \ln\left(\frac{p_i}{p_f}\right) = \left(\frac{25\,\text{g}}{16.04\,\text{g mol}^{-1}}\right) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{18.5\,\text{atm}}{2.5\,\text{atm}}\right)$$

$$= \boxed{+26\,\text{J K}^{-1}}$$

E4.12(b)

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{q_{rev}}{T} \quad \text{where } q_{rev} = -w = nRT \ln\frac{V_f}{V_i} = nRT \ln\frac{p_i}{p_f}$$

$$\text{so } \Delta S = nR \ln\frac{p_i}{p_f} = \left(\frac{35\,\text{g}}{28.013\,\text{g mol}^{-1}}\right) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\frac{21.1\,\text{atm}}{4.3\,\text{atm}} = \boxed{17\,\text{J K}^{-1}}$$

Answer 10.10

n/a	n/a	n/a

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

E4.13(a)

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) \text{ [4.17]}$$

The number of moles (or nR) and then V_f need to be determined

$$nR = \frac{p_i V_i}{T_i} = \frac{(1.00\,\text{atm}) \times (15.0\,\text{L})}{250\,\text{K}} = \frac{(1.01\bar{3} \times 10^5\,\text{Pa}) \times (15.0 \times 10^{-3}\,\text{m}^3)}{250\,\text{K}} = 6.08\,\text{J K}^{-1}$$

$$\ln\frac{V_f}{V_i} = \frac{\Delta S}{nR} = \frac{-5.0\,\text{J K}^{-1}}{6.08\,\text{J K}^{-1}} = -0.82\bar{3}$$

Hence, $V_f = V_i e^{-0.82\bar{3}} = (15.0\,\text{L}) \times (0.43\bar{9}) = \boxed{6.6\,\text{L}}$

E4.13(b)

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{q_{rev}}{T} \quad \text{where } q_{rev} = -w = nRT \ln\frac{V_f}{V_i}$$

$$\text{so } \Delta S = nR \ln\frac{V_f}{V_i} \text{ and } V_f = V_i \exp\left(\frac{\Delta S}{nR}\right)$$

We need to compute the amount of gas from the perfect gas law

$$pV = nRT \quad \text{so} \quad n = \frac{pV}{RT} = \frac{(1.20\,\text{atm}) \times (11.0\,\text{L})}{(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (270\,\text{K})} = 0.596\,\text{mol}$$

$$\text{So } V_f = (11.0\,\text{L}) \exp\left(\frac{-3.0\,\text{J K}^{-1}}{(0.596\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}\right) = \boxed{6.00\,\text{L}}$$

Answers:
Ex. 4.9a, 7th edition
12.9 J K^{-1}
Ex. 4.9b, 7th edition
76.9 J K^{-1}
Ex. 4.10a, 7th edition
not reversible
Ex. 4.10b, 7th edition
not reversible
Ex. 4.11a, 7th edition
(a) -58.2 kJ (b) -193 J K^{-1}
Ex. 4.11b, 7th edition
(a) -54.9 kJ (b) -195 J K^{-1}

Ex. 4.12a, 7th edition
26 J K^{-1}
Ex. 4.12b, 7th edition
17 J K^{-1}
Ex. 4.13a, 7th edition
6.6 L
Ex. 4.13b, 7th edition
6.0 L

A-list answers for the 9th edition:
3.1 (a) 92 J K^{-1}; (b) 67 J K^{-1}
3.2 152.67 J K^{-1} mol^{-1}
3.3 -22.1 J K^{-1}
3.4 $q = 0$, $\Delta S = 0$, $\Delta U = +4.1$ kJ, $w = +4.1$ kJ, $\Delta H = 5.4$ kJ
3.5 $\Delta H_{tot} = 0$, $\Delta S_{tot} = 93.4$ J K^{-1}