

Assigned questions for Lecture 7 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. **Updates are highlighted in yellow.**

Set 1

Question 7.01

2A.4	2.3	2.3
------	-----	-----

Variations in 8th and 9th vs. 10th edition questions:

2.3 (8th, 9th Eds.) (a) A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm³ to 44.8 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .

2.3 (8th, 9th Eds.) (b) A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm³ to 31.7 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .

2A.4 (10th Ed.) (a) A sample consisting of 1.00 mol Ar is expanded isothermally at 20°C from 10.0 dm³ to 30.0 dm³ (i) reversibly, (ii) against a constant external pressure equal to the final pressure of the gas, and (iii) freely (against zero external pressure). For the three processes calculate q , w , and ΔU .

2A.4 (10th Ed.) (b) A sample consisting of 2.00 mol He is expanded isothermally at 0°C from 5.0 dm³ to 20.0 dm³ (i) reversibly, (ii) against a constant external pressure equal to the final pressure of the gas, and (iii) freely (against zero external pressure). For the three processes calculate q , w , and ΔU .

Question 7.02

2B.2	2.8	2.8
------	-----	-----

Slight variation in 10th edition questions; calculate q , w , ΔU , and ΔH , no matter what edition you are using.

2B.2(a) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(J K^{-1}) = 20.17 + 0.3665(T/K)$. Calculate q , w , ΔU , and ΔH when the temperature is raised from 25°C to 200°C (a) at constant pressure, (b) at constant volume. **Note:** the temperature range in the 10th edition is 25°C to 100°C for some reason.

2B.2(b) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with

temperature according to the expression $C_p/(\text{J K}^{-1}) = 20.17 + 0.4001(T/\text{K})$. Calculate q , w , ΔU , and ΔH when the temperature is raised from 0°C to 100°C (a) at constant pressure, (b) at constant volume.

Question 7.03

2E.2	2.9	2.9
------	-----	-----

2E.2(a) Calculate the final temperature of a sample of argon of mass 12.0 g that is expanded reversibly and adiabatically from 1.0 dm^3 at 273.15 K to 3.0 dm^3 .

2E.2(b) Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 dm^3 at 298.15 K to 2.00 dm^3 .

Question 7.04

2E.4	2.10	2.10
------	------	------

2E.4(a) A sample of carbon dioxide of mass 2.45 g at 27.0°C is allowed to expand reversibly and adiabatically from 500 cm^3 to 3.00 dm^3 . What is the work done by the gas?

2E.4(b) A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from 400 cm^3 to 2.00 dm^3 . What is the work done by the gas?

Question 7.05

2E.5	2.11	2.11
------	------	------

Variation in 8th and 9th editions vs. 10th edition questions

2.11(8th, 9th Eds.) (a) Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 57.4 kPa and 1.0 dm^3 to a final volume of 2.0 dm^3 . Take $\gamma = 1.4$.

2.11(8th, 9th Eds.) (b) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 cm^3 to a final volume of 3.0 dm^3 . Take $\gamma = 1.3$.

2E.5 (10th Ed.) (a) Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 67.4 kPa and 0.50 dm^3 to a final volume of 2.00 dm^3 . Take $\gamma = 1.4$.

2E.5 (10th Ed.) (b) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 97.3 Torr and 400 cm^3 to a final volume of 5.0 dm^3 . Take $\gamma = 1.3$.

Question 7.06

n/a	n/a	n/a
-----	-----	-----

Yet another good problem which seems to be missing.

(Ex. 2.18a, 7th Ed.) Calculate the final pressure of a sample of carbon dioxide of mass 2.4 g that expands reversibly and adiabatically from an initial temperature of 287 K and a volume of 1.0 L to a final volume of 2.0 L . Take $\gamma = 1.4$.

Question 7.07

2B.1	2.12	2.12
------	------	------

2B.1(a) When 229 J of energy is supplied as heat to 3.0 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

2B.1(b) When 178 J of energy is supplied as heat to 1.9 mol of gas molecules, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

Set 2**Question 7.08**

n/a	n/a	n/a
-----	-----	-----

Yet another good problem which seems to be missing.

(Ex. 2.21a, 7th Ed.) A sample of liquid of mass 25 g is cooled from 290 K to 275 K at constant pressure by the extraction of 1.2 kJ energy as heat. Calculate q and ΔH and estimate the heat capacity of the sample.

Question 7.09

2B.3	2.13	2.13
------	------	------

2B.3(a) When 3.0 mol O₂ is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O₂ at constant pressure is 29.4 J K⁻¹ mol⁻¹, calculate q , ΔH , and ΔU .

2B.3(b) When 2.0 mol CO₂ is heated at a constant pressure of 1.25 atm, its temperature increases from 250 K to 277 K. Given that the molar heat capacity of CO₂ at constant pressure is 37.11 J K⁻¹ mol⁻¹, calculate q , ΔH , and ΔU .

Question 7.10

n/a	2.14	2.14
-----	------	------

This question seems to be missing from 10th Ed.

2.14(a) A sample of 4.0 mol O₂(g) is originally confined in 20 dm³ at 270 K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3.0. Calculate q , w , ΔT , ΔU , and ΔH . (The final pressure of the gas is not necessarily 600 Torr.)

2.14(b) A sample of 5.0 mol CO₂(g) is originally confined in 15 dm³ at 280 K and then undergoes adiabatic expansion against a constant pressure of 78.5 kPa until the volume has increased by a factor of 4.0. Calculate q , w , ΔT , ΔU , and ΔH . (The final pressure of the gas is not necessarily 78.5 kPa.)

Question 7.11

n/a	n/a	n/a
-----	-----	-----

(Ex. 2.24a, 7th Ed.) A sample consisting of 3.0 mol of perfect gas molecules at 200 K and 2.00 atm is compressed reversibly and adiabatically until the temperature reaches 250 K. Given that its molar constant volume heat capacity is $27.6 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔU and ΔH , as well as the final pressure and volume.

Question 7.12

2E.3	2.15	2.15
------	------	------

Slight variation between 8th and 9th editions vs. 10th edition (different numbers, same problems).

2.15(a) A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8 \text{ J K}^{-1}$ is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

2.15(b) A sample consisting of 1.5 mol of perfect gas molecules with $C_{p,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ is initially at 230 kPa and 315 K. It undergoes reversible adiabatic expansion until its pressure reaches 170 kPa. Calculate the final volume and temperature and the work done.

2E.3(a) A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8 \text{ J K}^{-1}$ is initially at 4.25 atm and 300 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

2E.3(b) A sample consisting of 2.5 mol of perfect gas molecules with $C_{p,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ is initially at 240 kPa and 325 K. It undergoes reversible adiabatic expansion until its pressure reaches 150 kPa. Calculate the final volume and temperature and the work done.

Question 7.13

n/a	n/a	n/a
-----	-----	-----

(Ex. 2.27a, 7th Ed.) Consider a system consisting of 2.0 mol of CO_2 (assumed to be a perfect gas, $C_{p,m} = 37.11 \text{ J K}^{-1} \text{ mol}^{-1}$) at 25°C confined to a cylinder of cross section 10 cm^2 at 10 atm. The gas is allowed to expand adiabatically and irreversibly against a constant pressure of 1.0 atm. Calculate q , w , ΔU and ΔH , as well as ΔT when the piston has moved 20 cm.

Question 7.14

n/a	n/a	n/a
-----	-----	-----

(Ex. 2.28a, 7th Ed.) A sample consisting of 65.0 g of xenon is confined to a container at 2.00 atm and 298 K and then allowed to expand adiabatically (a) reversibly to 1.00 atm and (b) against a constant pressure of 1 atm. Calculate the final temperature in each case.

Solution 7.06

n/a	n/a	n/a
-----	-----	-----

E2.18(a) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad [2.36] \quad \text{so} \quad p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma$$

We need p_i , which we can obtain from the perfect gas law

$$pV = nRT \quad \text{so} \quad p = \frac{nRT}{V}$$

$$p_i = \frac{\left(\frac{2.4 \text{ g}}{44 \text{ g mol}^{-1}} \right) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (278 \text{ K})}{1.0 \text{ L}} = \boxed{1.2 \text{ atm}}$$

$$p_f = (1.2 \text{ atm}) \times \left(\frac{1.0 \text{ L}}{2.0 \text{ L}} \right)^{1.4} = \boxed{0.45 \text{ atm}}$$

Solution 7.08

n/a	n/a	n/a
-----	-----	-----

E2.21(a) $q_p = \boxed{-1.2 \text{ kJ}}$ [energy left the sample] $\Delta H = q_p = \boxed{-1.2 \text{ kJ}}$

$$C_p = \frac{q_p}{\Delta T} = \frac{-1.2 \text{ kJ}}{-15 \text{ K}} = \boxed{80 \text{ J K}^{-1}}$$

Solution 7.10

n/a	2.14	2.14
-----	------	------

E2.14(a) In an adiabatic process, $q = 0$. Work against a constant external pressure is

$$w = -p_{\text{ex}}\Delta V = (-600 \text{ Torr}) \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{760 \text{ Torr}} \right) \times (40 \times 10^{-3} \text{ m}^3) = \boxed{-3.2 \text{ kJ}}$$

$$\Delta U = q + w = \boxed{-3.2 \text{ kJ}}$$

One can also relate adiabatic work to ΔT (eqn 2.27):

$$w = C_V \Delta T = n(C_{p,m} - R)\Delta T \quad \text{so} \quad \Delta T = \frac{w}{n(C_{p,m} - R)},$$

$$\Delta T = \frac{-3.2 \times 10^3 \text{ J}}{(4.0 \text{ mol}) \times (29.355 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}} = \boxed{-38 \text{ K}}$$

$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) = \Delta U + nR\Delta T \\ &= (-3.2 \text{ kJ}) + (4.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-38 \text{ K}) = \boxed{-4.5 \text{ kJ}} \end{aligned}$$

Question. Calculate the final pressure of the gas.

E2.14(b) In an adiabatic process, $q = 0$. Work against a constant external pressure is

$$w = -p_{\text{ex}}\Delta V = \frac{-(78.5 \times 10^3 \text{ Pa}) \times (4 \times 15 - 15) \text{ dm}^3}{(10 \text{ dm m}^{-1})^3} = \boxed{-3.5 \times 10^3 \text{ J}}$$

$$\Delta U = q + w = \boxed{-3.5 \times 10^3 \text{ J}}$$

One can also relate adiabatic work to ΔT (eqn 2.27):

$$w = C_V \Delta T = n(C_{p,m} - R)\Delta T \quad \text{so} \quad \Delta T = \frac{w}{n(C_{p,m} - R)},$$

$$\Delta T = \frac{-3.5 \times 10^3 \text{ J}}{(5.0 \text{ mol}) \times (37.11 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}} = \boxed{-24 \text{ K}}$$

$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) = \Delta U + nR\Delta T, \\ &= -3.5 \times 10^3 \text{ J} + (5.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-24 \text{ K}) = \boxed{-4.5 \times 10^3 \text{ J}} \end{aligned}$$

Solution 7.11

n/a	n/a	n/a
-----	-----	-----

Question. Calculate the final pressure of the gas.

E2.24(a) $q = 0$ [adiabatic process]
 $\Delta U = nC_{V,m}\Delta T$ [perfect gas] $= (3.0 \text{ mol}) \times (27.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times (50 \text{ K}) = +4.1 \text{ kJ}$
 $w = \Delta U - q = 4.1 \text{ kJ} - 0 = +4.1 \text{ kJ}$
 $\Delta H = \Delta U + nR\Delta T$ [$\Delta(pV) = \Delta(nRT) = nR\Delta T$]
 $= (4.1 \text{ kJ}) + (3.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (50 \text{ K}) = +5.4 \text{ kJ}$
 $V_i = \frac{nRT_i}{p_i} = \frac{(3.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K})}{(2.0 \text{ atm})} = 24.6 \text{ L}$
 $V_f = V_i \left(\frac{T_i}{T_f}\right)^c$ [2.34], $c = \frac{C_V}{R} = \frac{27.5 \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} = 3.31$

$$V_f = (24.6 \text{ L}) \times \left(\frac{200 \text{ K}}{250 \text{ K}}\right)^{3.31} = 11.8 \text{ L}$$

$$p_f = \frac{nRT_f}{V_f} = \frac{(3.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (250 \text{ K})}{11.8 \text{ L}} = 5.2 \text{ atm}$$

Solution 7.13

n/a	n/a	n/a
-----	-----	-----

E2.27(a) In an adiabatic process, $q = 0$. Work against a constant external pressure is

$$w = -p_{\text{ex}}\Delta V = -(1.0 \text{ atm}) \times (1.01 \times 10^5 \text{ Pa atm}^{-1}) \times \frac{(20 \text{ cm}) \times (10 \text{ cm}^2)}{(100 \text{ cm m}^{-1})^3} = -20 \text{ J}$$

$$\Delta U = q + w = -20 \text{ J}$$

$$w = C_V\Delta T = n(C_{p,m} - R)\Delta T \quad \text{so} \quad \Delta T = \frac{w}{n(C_{p,m} - R)},$$

$$\Delta T = \frac{-20 \text{ J}}{(2.0 \text{ mol}) \times (37.11 - 8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} = -0.35 \text{ K}$$

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

$$= -20 \text{ J} + (2.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-0.35 \text{ K}) = -26 \text{ J}$$

Solution 7.14

n/a	n/a	n/a
-----	-----	-----

E2.28(a) The amount of Xe in the sample is

$$n = \frac{65.0 \text{ g}}{131.3 \text{ g mol}^{-1}} = 0.495 \text{ mol}$$

(a) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{so} \quad V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma},$$

$$\text{where } \gamma = \frac{C_{p,m}}{C_{v,m}} \quad \text{where } C_{v,m} = (20.79 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1} = 12.48 \text{ J K}^{-1} \text{ mol}^{-1}.$$

$$\text{so } \gamma = \frac{20.79 \text{ J K}^{-1} \text{ mol}^{-1}}{12.48 \text{ J K}^{-1} \text{ mol}^{-1}} = 1.666,$$

$$\text{and } V_i = \frac{nRT_i}{p_i} = \frac{(0.495 \text{ mol}) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{2.00 \text{ atm}} = 6.05 \text{ L},$$

$$\text{so } V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma} = (6.05 \text{ L}) \times \left(\frac{2.00 \text{ atm}}{1.00 \text{ atm}} \right)^{(1/1.666)} = 9.17 \text{ L},$$

$$T_f = \frac{p_f V_f}{nR} = \frac{(1.00 \text{ atm}) \times (9.17 \text{ L})}{(0.495 \text{ mol}) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})} = \boxed{226 \text{ K}}$$

(b) For adiabatic expansion against a constant external pressure

$$w = -p_{\text{ex}} \Delta V = C_V \Delta T \quad \text{so} \quad -p_{\text{ex}}(V_f - V_i) = C_V(T_f - T_i)$$

In addition, the perfect gas law holds

$$p_f V_f = nRT_f$$

Solve the latter for T_f in terms of V_f , and insert into the previous relationship to solve for V_f

$$T_f = \frac{p_f V_f}{nR} \quad \text{so} \quad -p_{\text{ex}}(V_f - V_i) = C_V \left(\frac{p_f V_f}{nR} - T_i \right)$$

Collecting terms gives

$$C_V T_i + p_{\text{ex}} V_i = V_f \left(p_{\text{ex}} + \frac{C_V p_f}{nR} \right) \quad \text{so} \quad V_f = \frac{C_V T_i + p_{\text{ex}} V_i}{p_{\text{ex}} + \frac{C_V p_f}{nR}}$$

$$V_f = \frac{(12.48 \text{ J K}^{-1} \text{ mol}^{-1}) \times (0.495 \text{ mol}) \times (298 \text{ K}) + (1.00 \text{ atm}) \times (1.01 \times 10^5 \text{ Pa atm}^{-1}) \times \left(\frac{6.05 \text{ L}}{1000 \text{ L m}^{-3}} \right)}{\left(1.00 \text{ atm} + \frac{(12.48 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.00 \text{ atm})}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (1.01 \times 10^5 \text{ Pa atm}^{-1})}$$

$$V_f = 9.71 \times 10^{-3} \text{ m}^3$$

Finally, the temperature is

$$T_f = \frac{p_f V_f}{nR} = \frac{(1.00 \text{ atm}) \times (1.01 \times 10^5 \text{ Pa atm}^{-1}) \times (9.71 \times 10^{-3} \text{ m}^3)}{(0.495 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{238 \text{ K}}$$