

Assigned questions for Lecture 9 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
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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.

Question 9.01

2D.4	P2.30	P2.26
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2D.4(a) Write expressions for dV and dp given that V is a function of p and T and p is a function of V and T .

2D.4(b) Deduce expressions for $d \ln V$ and $d \ln p$ in terms of the expansion coefficient and the isothermal compressibility.

Question 9.02

n/a	n/a	n/a
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Question is missing from the 10th and earlier editions, back to the 7th Ed.

(Ex. 3.12a, 7th edition) Show that $(\partial p / \partial T)_V = \alpha / \kappa_T$.

(Ex. 3.12b, 7th edition) Evaluate α and κ_T for a perfect gas.

Question 9.03

n/a	2.30	2.29
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Question is missing from the 10th edition.

2.30(a) (9th), 2.29(a) (8th). When a certain freon used in refrigeration was expanded adiabatically from an initial pressure of 32 atm and 0°C to a final pressure of 1.00 atm, the temperature fell by 22 K. Calculate the Joule–Thomson coefficient, μ , at 0°C , assuming it remains constant over this temperature range.

2.30(b) (9th), 2.29(b) (8th). A vapour at 22 atm and 5°C was allowed to expand adiabatically to a final pressure of 1.00 atm; the temperature fell by 10 K. Calculate the Joule–Thomson coefficient, μ , at 5°C , assuming it remains constant over this temperature range.

Question 9.04

2D.2	2.31	2.30
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2D.2(a) For a van der Waals gas, $\pi_T = a/V_m^2$. Calculate ΔU_m for the isothermal expansion of nitrogen gas from an initial volume of 1.00 dm^3 to 20.00 dm^3 at 298 K. What are the values of q and w ? **Note:** in earlier editions, the expansion is 1.00 dm^3 to 24.8 dm^3 .

2D.2(b) Repeat the above question for argon, from an initial volume of 1.00 dm^3 to 30.00 dm^3 at 298 K. **Note:** in earlier editions, the expansion is 1.00 dm^3 to 22.1 dm^3 .

Question 9.05

2D.3	2.32	2.31
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2D.3(a) The volume of a certain liquid varies with temperature as

$$V = V' \{0.75 + 3.9 \times 10^{-4}(T/K) + 1.48 \times 10^{-6} (T/K)^2\}$$

where V' is its volume at 300 K. Calculate its expansion coefficient, α , at 320 K.

2D.3(b) The volume of a certain liquid varies with temperature as

$$V = V' \{0.77 + 3.7 \times 10^{-4} (T/K) + 1.52 \times 10^{-4}(T/K)^2\}$$

where V' is its volume at 298 K. Calculate its expansion coefficient, α , at 310 K.

Question 9.06

2D.4	2.33	2.32
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Slight variation in 10th edition vs. earlier editions.

2D.4(a) The isothermal compressibility of water at 293 K is $4.96 \times 10^{-5} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.10 per cent.

2D.4(b) The isothermal compressibility of lead at 293 K is $2.21 \times 10^{-6} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.10 per cent.

2.33(a) (9th), 2.32(a) (8th). The isothermal compressibility of copper at 293 K is $7.35 \times 10^{-7} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

2.33(b) (9th), 2.32(b) (8th). The isothermal compressibility of lead at 293 K is $2.21 \times 10^{-6} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

Question 9.07

2D.5	2.34	2.33
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Slight variation in 10th edition vs. earlier editions.

2D.5(a) Given that $\mu = 0.25 \text{ K atm}^{-1}$ for nitrogen, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 10.0 mol N_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 85 atm.

2D.5(b) Given that $\mu = 1.11 \text{ K atm}^{-1}$ for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 10.0 mol CO_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

2.34(a) (9th), 2.33(a) (8th). Given that $\mu = 0.25 \text{ K atm}^{-1}$ for nitrogen, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 15.0 mol N_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

2.34(b) (9th), 2.33(b) (8th). Given that $\mu = 1.11 \text{ K atm}^{-1}$ for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 12.0 mol CO_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 55 atm.

Question 9.08

n/a	n/a	n/a
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Question is missing from all editions, this is from the 7th edition.

(Ex. 3.18a, 7th edition) To design a particular kind of refrigerator, we need to know the temperature reduction brought about by adiabatic expansion of the refrigerant gas. For one type of freon, $\mu = 1.2 \text{ K atm}^{-1}$. What pressure difference is needed to provide a temperature drop of 5.0 K?

Question 9.09

n/a	P2.25	P2.23
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Question is missing from the 10th edition.

P2.25(9th), P2.23 (8th). Derive the relation $C_V = -(\partial U/\partial V)_T(\partial V/\partial T)_U$ from the expression for the total differential of $U(T,V)$ and (b) starting from the expression for the total differential of $H(T,p)$, express $(\partial H/\partial p)_T$ in terms of C_p and the Joule–Thomson coefficient, μ .

Question 9.10

n/a	P2.26	P2.24
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Note: In some earlier editions, There is a typo in the question. In the denominator of the expression you are being asked to show, it should be $(dV/dp)_T$, not $(dV/dT)_T$ (the latter does not make any sense).

2D.3 Starting from the expression $C_p - C_V = T(\partial p/\partial T)_V(\partial V/\partial T)_p$, use the appropriate relations between partial derivatives to show that:

$$C_p - C_V = \frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T}$$

Evaluate $C_p - C_V$ for a perfect gas.

Question 9.11

P2D.9	P2.34	P2.30
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2D.9 Use the fact that $(\partial U/\partial V)_T = a/V_m^2$ for a van der Waals gas to show that $\mu C_{p,m} \approx (2a/RT) - b$ by using the definition of μ and appropriate relations between partial derivatives. (*Hint.* Use the approximation $pV_m \approx RT$ when it is justifiable to do so.)

Question 9.12

n/a	P2.38	P2.34
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Question is missing from the 10th edition.

P2.38 (9th), P2.34 (8th). The thermodynamic equation of state $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$ was quoted in the chapter. Derive its partner

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

from it and the general relations between partial differentials.

Solution 9.02

n/a	n/a	n/a
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(Ex. 3.12a, 7th edition)

E3.12(a) $V = V(T, p)$; hence, $dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$

Dividing each term by $(dT)_V$ we obtain

$$\left(\frac{\partial V}{\partial T}\right)_V = 0 = \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial T}\right)_V + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$\text{or } 0 = \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$\text{or } \left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p}{-\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha}{\kappa_T}$$

(Ex. 3.12b, 7th edition)

E3.12(b) $\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p$ $V = \frac{nRT}{p}$ $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} = \frac{V}{T}$

$$\alpha = \left(\frac{1}{V}\right) \times \left(\frac{V}{T}\right) = \boxed{\frac{1}{T}}$$

Solution 9.03

n/a	2.30	2.29
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2.30(a) (9th), 2.29(a) (8th).

E2.30(a) The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H [2.50] = \lim_{\Delta p \rightarrow 0} \left(\frac{\Delta T}{\Delta p} \right)_H \approx \frac{\Delta T}{\Delta p} [\mu \text{ constant over temperature range}]$$

$$\mu = \frac{-22 \text{ K}}{-31 \text{ atm}} = \boxed{0.71 \text{ K atm}^{-1}}$$

2.30(b) (9th), 2.29(b) (8th).

E2.30(b) The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So,

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-10 \text{ K}}{(1.00 - 22) \text{ atm}} = \boxed{0.48 \text{ K atm}^{-1}}$$

Solution 9.08

n/a	n/a	n/a
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Note: In an exam question, you would be guided with the assumption that the pressure and temperature changes are small.

(Ex. 3.18a, 7th edition)

$$\mathbf{E3.18(a)} \quad \mu = \left(\frac{\partial T}{\partial p} \right)_H = \lim_{\Delta p \rightarrow 0} \left(\frac{\Delta T}{\Delta p} \right)$$

If Δp is not so large as to produce a ΔT which is a large fraction of T we may write approximately

$$\mu \approx \frac{\Delta T}{\Delta p} \quad \text{or} \quad \Delta p \approx \frac{\Delta T}{\mu}$$

For $\Delta T = -5.0 \text{ K}$,

$$\Delta p \approx \frac{-5.0 \text{ K}}{1.2 \text{ K atm}^{-1}} = \boxed{-4.2 \text{ atm}}$$

Solution 9.09

n/a	P2.25	P2.23
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P2.25(9th), P2.23 (8th).

$$\text{P2.25} \quad (\text{a}) \quad U = U(T, V) \quad \text{so} \quad dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

For $U = \text{constant}$, $dU = 0$, and

$$C_V dT = - \left(\frac{\partial U}{\partial V} \right)_T dV \quad \text{or} \quad C_V = - \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{dV}{dT} \right)_U = - \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_U$$

This relationship is essentially Euler's chain relationship [MB2.4].

$$(\text{b}) \quad H = H(T, p) \quad \text{so} \quad dH = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp = C_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

According to Euler's chain relationship

$$\left(\frac{\partial H}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_H \left(\frac{dT}{dH} \right)_p = -1$$

so, using the reciprocal identity [MB2.3c],

$$\left(\frac{\partial H}{\partial p} \right)_T = - \left(\frac{\partial T}{\partial p} \right)_H \left(\frac{dH}{dT} \right)_p = -\mu C_p.$$

Solution 9.12

n/a	P2.38	P2.34
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It should be mentioned that the relation $\pi_T = T(dp/dT)_V - p$ will be useful in solving this problem. This equation is discussed a few pages prior to the question in all editions. *Note that the answer to this problem and other related problems are available on the downloads page - just download all of these and look up the appropriate problem numbers.*

P2.38 (9th), P2.34 (8th).

P2.38 Work with the left-hand side of the relationship to be proved and show that after manipulation using the general relationships between partial derivatives and the given equation for $\left(\frac{\partial U}{\partial V}\right)_T$, the right-hand side is produced.

$$\begin{aligned}
 \left(\frac{\partial H}{\partial p}\right)_T &= \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T \text{ [change of variable]} \\
 &= \left(\frac{\partial(U + pV)}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T \text{ [definition of } H\text{]} \\
 &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial(pV)}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T \\
 &= \left\{ T \left(\frac{\partial p}{\partial T}\right)_V - p \right\} \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial(pV)}{\partial p}\right)_T \left[\text{equation for } \left(\frac{\partial U}{\partial V}\right)_T \right] \\
 &= T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T - p \left(\frac{\partial V}{\partial p}\right)_T + V + p \left(\frac{\partial V}{\partial p}\right)_T \\
 &= T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T + V = \frac{-T}{\left(\frac{\partial T}{\partial V}\right)_p} + V \text{ [chain relation]} \\
 &= \boxed{-T \left(\frac{\partial V}{\partial T}\right)_p} + V \text{ [reciprocal identity]}
 \end{aligned}$$