

GCE

Chemistry A

H432/03: Unified chemistry

Advanced GCE

Mark Scheme for Autumn 2021

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All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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1. Annotations

Annotation	Meaning
✓	Correct response
X	Incorrect response
^	Omission mark
BOD	Benefit of doubt given
CON	Contradiction
RE	Rounding error
SF	Error in number of significant figures
ECF	Error carried forward
Li	Level 1
L2	Level 2
L3	Level 3
NBOD	Benefit of doubt not given
SEEN	Noted but no credit given
I	Ignore

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2. Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
_	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

Question	Answer	Marks	AO element	Guidance
1 (a)	FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 20 award 2 marks $n(CO_2) = \frac{110}{44} \text{ OR } 2.5 \text{ (mol)}$ AND $n(O_2) = \frac{120}{32} \text{ OR } 3.75 \text{ (mol)} \checkmark$	2	AO1.2 × 2	
	$p(CO_2) = \frac{2.5}{6.25} \times 50.0 \text{ OR } 0.4 \times 50.0 = 20(.0) \text{ (atm) } \checkmark$			ALLOW ECF from incorrect Σ ($n(CO_2) + n(O_2)$) ONLY
(b)	FIRST CHECK THE ANSWER ON ANSWER LINES If [PCI ₃] = [CI ₂] = 0.02(00) award 2 marks $ K_c = \frac{[PCI_3] [CI_2]}{[PCI_5]} \text{ OR with number(s), e.g. } K_c = \frac{[PCI_3] [CI_2]}{0.05(00)} \checkmark $ $ [PCI3] = [CI2] = \sqrt{(K_c \times [PCI_5])} $ $ = \sqrt{(8.00 \times 10^{-3} \times 0.0500)} $ $ = \sqrt{(4.00 \times 10^{-4})} $ $ = 2.00 \times 10^{-2} \text{ (mol dm}^{-3}) \checkmark $	2	AO1.1	Square brackets required Common errors 2.00×10^{-4} from $K_c = \frac{[PCl_3] [Cl_2]}{[PCl_5]}$ 1 mark $\div 2 \text{ instead of } $ 2.5 from $K_c = \frac{[PCl_5]}{[PCl_3] [Cl_2]}$ 1 mark Inverse K_c expression

Question	Answer	Marks	AO element	Guidance
	Electronegativity and boiling point Boiling point/Energy increases with increased electronegativity (difference) ✓	3	AO1.1	ANNOTATE WITH TICKS AND CROSSES ALLOW ORA throughout ORA
	Type of intermolecular force HF AND NH₃ have hydrogen bonding AND CH₄ has London forces/induced (dipole–)dipole interactions ✓		AO1.2	IGNORE permanent dipole interactions IGNORE IDID IGNORE HF and NH₃ are polar/CH₄ is non-polar
	Comparison between strength of intermolecular forces HF has stronger hydrogen bonding than NH₃ OR hydrogen bonding is stronger than London forces ✓		AO2.1	IGNORE strength of ionic and covalent bonds
(d)	 A: Ca₃N₂ (formula required) ✓ B: NH₃ OR ammonia ✓ C: Ca(OH)₂ OR calcium hydroxide ✓ Equation: Ca₃N₂ + 6H₂O → 2NH₃ + 3Ca(OH)₂ ✓ 	4	AO1.1 AO2.7 ×2 AO2.6	IGNORE working If B and C labels are the wrong way round OR missing, award 1/2 for B and C labels, i.e. for B Ca(OH) ₂ C NH ₃ 1/2 marks ALLOW CaO ₂ H ₂ ALLOW multiples for equation IF C = CaO, ALLOW ECF for: Ca ₃ N ₂ + 3H ₂ O → 2NH ₃ + 3CaO

(e) 4	 element	
2CH ₃ CH(OH)COOH + Na ₂ CO ₃ → 2CH ₃ CH(OH)COONa + CO ₂ + H ₂ O CO ₂ and H ₂ O OR CH ₃ CH(OH)COONa as product(s) Balanced equation correct ✓ 3CH ₃ CH(OH)COOH + AI → (CH ₃ CH(OH)COO) ₃ AI + 1½ H ₂ H ₂ OR (CH ₃ CH(OH)COO) ₃ AI as product ✓ Balanced equation correct ✓	AO2.6 ×4	ALLOW multiples IGNORE state symbols ALLOW ions shown separately For CO ₂ AND H ₂ O, ALLOW H ₂ CO ₃ ALLOWCOONa ⁺ (i.e. one of charges missing) ALLOWCOO) ₃ Al ³⁺ (i.e. one of charges missing)

Question	Answer	Marks	AO element	Guidance
(f)	Mechanism: H CH ₃ COO ⁻ NOTE: Can be any C-X bond, e.g. C-Cl, C-Br, C-I but must be consistent. Curly arrow on C-X Dipole shown on C-X bond of CH ₃ X, C ^{δ+} and X ^{δ-} AND curly arrow from C-X bond to X atom ✓ Curly arrow from CH ₃ COO ⁻	3	AO2.5 AO1.2	ANNOTATE ANSWER TICKS AND CROSSES NOTE: Curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows 1st curly arrow must start from, OR be traced back to, any part of C-Cl bond and go to Cl C-Cl C-Cl 2nd curly arrow must • go to the C of C-Cl AND • start from, OR be traced back to any point across width of lone pair on O of CH ₃ COO- CH ₃ COO-CH ₃ COO-CH ₃ COO-CH ₃ COO- OR start from '-' on O of CH ₃ COO-ion (Lone pair NOT needed if curly arrow from O-) If CH ₃ COOH used instead of CH ₃ COO-, ALLOW X-OR HX as 2nd product

Question	Answer	Marks	AO element	Guidance
				ALLOW S _N 1 mechanism First mark Dipole shown on C–Cl bond, C ^{δ+} and Cl ^{δ−} , AND curly arrow from C–Cl bond to Cl atom ✓ H C H C C H C H C H C H C H C C

Question	Answer	Marks	AO element	Guidance
2 (a)	Reaction apparatus with tube/side arm AND gas collection apparatus AND closed system ✓ Labels Reaction apparatus, e.g.: Conical flask, Buchner flask/conical flask with side arm, test-tube, boiling tube. AND Gas collection apparatus: (gas) syringe OR gas collection over water with labelled measuring cylinder / burette ✓	2	AO3.3 × 2	ALLOW small gaps provided there is an attempt to show closed system DO NOT ALLOW delivery tube below reaction mixture For reaction apparatus, • DO NOT ALLOW flask, volumetric flask, beaker, measuring cylinder • Delivery tube, bung does NOT need a label ALLOW labels for diagram without closed system (e.g. bung missing), i.e. 2nd mark but not 1st mark ALLOW any of these diagrams. ALLOW a single line for the tube IGNORE Sealed end of delivery tube IGNORE size of syringe/measuring cylinder/burette

Question	Answer	Marks	AO element	Guidance
(b)	$n(H_2) = \frac{152}{24000}$ OR 6.33×10^{-3} (mol) \checkmark $n(Eu) = \frac{0.988}{152}$ OR $6.5(0) \times 10^{-3}$ (mol) \checkmark Ratio $H_2 : Eu$ 1 : 1 AND Equation 2 is correct \checkmark Only ALLOW if $n(H_2)$ AND $n(Eu)$ are approximately equal ALLOW use of ideal gas equation at a reasonable temperature and pressure. e.g. Using 100 kPa and 298 K, $n(H_2) = 6.14 \times 10^{-3}$ mol	3	AO2.8 ×2 AO3.2 ×1	152 $6.5(0) \times 10^{-3}$ (mol) ALLOW $0.97(4) : 1$ ALLOW ECF from incorrect $n(Eu)$ OR/AND $n(H_2)$ ———————————————————————————————————

Question	Answer	Marks	AO element	Guidance
(c)	The gas volume would be larger (than at RTP) ✓ Ratio H₂: Eu would be larger ✓	2	AO3.4 ×2	IGNORE effect of rate, e.g. rate increases IGNORE gas equation should be used to find $n(H_2)$ ALLOW Equation 3 linked to H_2 : Eu > 1
(d)	Precipitates have different molar masses OR Precipitates have different formulae ✓ Quant Equation 2 forms precipitate with M = 186 OR with formula Eu(OH) ₂ OR Equation 2 forms 1.86 g precipitate OR Molar mass M of precipitate = mass of precipitate moles precipitate OR Mass of precipitate moles Eu OR Mass of precipitate OR Mass of precipitate	2	AO3.4 ×2	ALLOW precipitates are EuOH, Eu(OH) ₂ Eu(OH) ₃ OR precipitates have different number of OH ⁻ ions ALLOW Moles OH ⁻ = mass of precipitate – mass of Eu molar mass of OH ⁻ OR Moles OH ⁻ = mass of precipitate –1.52 17

C	Questio	Answer	Marks	AO element	Guidance
3	(a)	n(Ba(OH)₂) = 0.150 × 250/1000 OR 0.0375 (mol) ✓ Mass Ba(OH)₂ = 0.0375 × 171.3 = 6.42375 (g) ✓ Dissolve solid in (distilled) water (less than 250 cm³) in beaker ✓ Transfer (solution) to volumetric flask AND Transfer washings (from beaker) to flask ✓ Make up to mark/up to 250 cm³ with (distilled) water AND Invert flask (several times to ensure mixing) ✓	5	AO2.4 ×2 AO1.2 ×3	ALLOW ECF from incorrect n(Ba(OH) ₂) ALLOW 6.42 up to 6.42375 correctly rounded 6.42 g subsumes 1st mark ALLOW conical flask for beaker ALLOW graduated flask DO NOT ALLOW round-bottom or conical flask
	(b)	$n(Ba(OH)_2) = 0.150 \times \frac{23.50}{1000}$ $= 3.525 \times 10^{-3} \text{ (mol)} \checkmark$ $n(\mathbf{D}) \text{ in } 25.0 \text{ cm}^3 = 2 \times 3.525 \times 10^{-3}$ $= 7.05 \times 10^{-3} \text{ (mol)} \checkmark$ $n(\mathbf{D}) \text{ in } 100 \text{ cm}^3 = 7.05 \times 10^{-3} \times \frac{100}{25.0}$ $= 0.0282 \text{ (mol)} \checkmark$ $Molar \text{ mass } (\mathbf{D}) = \frac{3.215}{0.0282} = 114 \text{ (g mol}^{-1}) \checkmark$	7	AO2.8 ×4	Use ECF throughout Intermediate values for working to at least 3 SF. TAKE CARE as value written down may be truncated value stored in calculator. Depending on rounding, either can be credited. ALLOW Mass D in 25.0 cm ³ = $\frac{3.215}{4}$ = 0.80375 g
		Formula: = C_5H_9COOH OR C_nH_{2n-1} : $M(C_5H_9)$ = 114 – 45 = 69 \checkmark If not stated, could be credited from structure		AO3.2 ×1	Molar mass (D) = $\frac{0.80375}{7.05 \times 10^{-3}}$ = 114

Question	Answer	Marks	AO element	Guidance
Question	cis stereoisomers. The drawn stereoisomers must have • Different groups attached to each C atom of C=C • Each C of C=C has the same group on the same side Any 2 cis isomers ✓ Many possibilities, e.g. H ₃ C CH ₂ CH ₂ COOH CH ₃ CH ₂ CH ₂ COOH CH ₃ CH ₂ CH ₂ COOH CH ₃ CH ₂ CH ₂ COOH H CH ₃ CH ₂ CH ₂ COOH H CH ₃ CH ₂ CH ₂ COOH H CH ₂ COOH CH ₂ COOH	Marks	_	COMMON ERRORS: Up to Molar mass = 114 (1st 4 marks) $M = 456 \rightarrow 3/4$ marks (mol in 100 cm³ omitted) $M = \frac{3.215}{7.05 \times 10^{-3}} = 456$ $M = 228 \rightarrow 3/4$ marks (No × 2 for n(D)) $3.525 \times 10^{-3} \times \frac{100}{25.0} = 0.0141$ $M = \frac{3.215}{0.0141} = 228$ $M = 100.8 \rightarrow 3/4$ marks 23.50 instead of 25.00 and scaling by × $\frac{100}{23.50}$ $25.0 \times \frac{0.150}{1000} = 3.75 \times 10^{-3} \times 10^{-$
	OR displayed formula OR mixture of above as long as non-ambiguous			calculated M (alkyl group) but must be C_nH_{2n-1} e.g. For M (alkyl) = 100, ALLOW C_4H_7 (55) For M (alkyl) = 411, ALLOW $C_{29}H_{57}$ (405) OR $C_{30}H_{59}$ (419)
	ALLOW side chains as molecular formula, e.g. C ₃ H ₇ for (CH ₃) ₂ CH OR CH ₃ CH ₂ CH ₂ e.g. C ₃ H ₅ O ₂ for CH ₂ CH ₂ COOH			THEN judge <i>cis</i> isomers with closest match ALLOW 1 mark for 2 <i>trans</i> isomers shown
	IGNORE poor connectivity to all groups			instead of 2 <i>cis</i> isomers ECF for Same error made twice.

	Questio	Answer	Marks	AO element	Guidance
4	(a)	(Large) excess of pent-1-ene OR There is a (large) excess ✓	1	AO3.1	ALLOW pent-1-ene concentration is (much) greater OR pent-1-ene has a high concentration
	(b)	Please refer to the marking instructions on page 6 of this mark scheme for guidance on how to mark this question. Level 3 (5–6 marks) Obtains a comprehensive conclusion to determine initial rate AND order AND rate constant k There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated. Level 2 (3–4 marks) Obtains a sound, but not comprehensive conclusion, to determine initial rate AND order OR order AND rate constant k OR initial rate AND rate constant k There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. Level 1 (1–2 marks) Obtains a simple conclusion to determine initial rate OR order	6	AO3.1 ×4 AO3.2 ×2	Initial rate Evidence of tangent on graph drawn to line at t = 0 s AND gradient determined in range 4.5 - 6.5 × 10 ⁻⁶ initial rate expressed as gradient value with units of mol dm ⁻³ s ⁻¹ , e.g. initial rate = 5.5 × 10 ⁻⁶ mol dm ⁻³ s ⁻¹ Reasoned order of I ₂ Half lives Half life measured on graph OR within text OR stated in range 2500 ±10 s Constant half life OR two stated half lives within ±10 s AND conclusion that I ₂ is 1st order OR Comparison of rates from gradients Rate measured as gradient at a concentration, c Rate measured at c/2
		There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. O marks No response or no response worthy of credit.			 c halves and rate halves so order 1 e.g. initial rate at c = 0.02 = 5.5 × 10⁻⁶ mol dm⁻³ s⁻¹ rate at c = 0.01 = 2.58 × 10⁻⁶ mol dm⁻³ s⁻¹

Que	estion	Answer	Marks	AO element	Guidance
(4	;) (i)	Reactants for 1st step: CH ₃ CH ₂ CH ₂ CH=CH ₂ + I ₂ ✓ 2 steps that add up to overall equation: CH ₂ CH ₂ CH=CH ₂ + I ₂ → CH ₃ CH ₂ CH ₂ CHICH ₂ I ✓ e.g. CH ₃ CH ₂ CH=CH ₂ + I ₂ → CH ₃ CH ₂ CH ₂ CHICH ₂ + + I ⁻	2	AO2.5 × 2	 Determination of <i>k</i> with units Rate constant <i>k</i> clearly linked to initial rate OR half-life: k = rate I2 OR k = ln 2 / t1/2 k determined correctly from measured initial rate or measured half life with units of s⁻¹, e.g. k = 5.5 × 10⁻⁶ / 0.02 = 2.75 × 10⁻⁴ s⁻¹ from initial rate of 5.5 × 10⁻⁶ mol dm⁻³ s⁻¹ OR from t1/2 of 2500 s Typical range 2.25–3.25 × 10⁻⁴ ALLOW mechanism for electrophilic addition shown. IGNORE state symbols Must be based on slow step, i.e. 2nd mark dependent on correct slow step: CH₃CH₂CH₂CH=CH₂ + I₂
		$CH_3CH_2CH_2CHICH_2^+ + I^- \rightarrow CH_3CH_2CH_2CHICH_2I$			IGNORE actual positioning of + charge
	(ii)	Repeat experiment with [I ₂] constant/kept the same OR use (large) excess of I ₂ ✓ Monitor/measure/plot [CH ₃ CH ₂ CH ₂ CH=CH ₂] over time OR Monitor/measure how [CH ₃ CH ₂ CH ₂ CH=CH ₂] affects rate ✓	2	AO3.4 ×2	ALLOW In (great) excess ALLOW initial rates approach of running several experiments with different concentrations of CH₃CH₂CH=CH₂ i.e. Measure initial rates for each experiment AND double concentration → rate doubles

Question	Answer	Marks	AO element	Guidance
5 (a) (i) (ii)	Reduction: Na ⁺ + e ⁻ \rightarrow Na \checkmark Oxidation: $2N_3^- \rightarrow 3N_2 + 2e^- \checkmark$ ALLOW 1 mark for 2 correct equations but wrong way round FIRST CHECK ANSWER ON ANSWER LINE	5	AO1.2	ALLOW multiples e.g. 2Na ⁺ + 2e ⁻ → 2Na IGNORE state symbols TAKE CARE as value written down may be
	IF mass = 34.5 (g) AND working using ideal gas equation Award 5 marks for calculation Rearranging ideal gas equation $n = \frac{pV}{RT} \checkmark$ Unit conversion AND substitution into $n = \frac{pV}{RT}$: • $R = 8.314$ OR 8.31 • $V = 16(.0) \times 10^{-3}$ • T in K : 290 K e.g. $\frac{1.20 \times 10^5 \times 16.0 \times 10^{-3}}{8.314 \times 290}$ Calculation of n $n = 0.796$ (mol) \checkmark Calculation of mass $n(\text{NaN}_3) = \frac{2}{3} \times 0.796 = 0.531$ (mol) \checkmark mass $\text{NaN}_3 = 0.531 \times 65 = 34.5$ (g) \checkmark 3 SF required		AO2.4 ×5	truncated value stored in calculator. IF $n = \frac{pV}{RT}$ is omitted, ALLOW when values are substituted into rearranged ideal gas equation. Calculator: 0.7963302448 From unrounded 0.7963302448, $n(\text{NaN}_3) = 0.5308868299$ mass = 0.5308868299 × 65 = 34.50764394 \rightarrow 34.5 to 3 SF COMMON ERROR 51.7 OR 51.8 \rightarrow 4 marks (2/3 omitted depending on intermediate rounding 0.796 × 65 = 51.7 OR 51.8 54.4 \rightarrow 4 marks (inverted gas equation) $n = \frac{RT}{pV} \rightarrow$ 1.255760417 \rightarrow 0.8371736111 \rightarrow 54.4 (g) CARE with intermediate rounding 81.6 OR 81.7 \rightarrow 3 mks (as above but no 2/3)

Question	Answer	Marks	AO element	Guidance
(b) (i)	FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 2.75 award 2 marks $[H^{+}]^{2} = K_{a} \times [HN_{3}]) = 2.51 \times 10^{-5} \times 0.125$ $[H^{+}]^{2} = 2.51 \times 10^{-5} \times 0.125$ $OR [H^{+}] = \sqrt{(2.51 \times 10^{-5} \times 0.125)}$ $OR [H^{+}] = 1.77 \times 10^{-3} \text{ (mol dm}^{-3}) \checkmark$ $pH = -\log 1.77 \times 10^{-3} = 2.75 \text{ (Must be to 2DP)} \checkmark$	2	AO2.2 ×2	ALLOW ECF throughout IGNORE error with HN ₃ shown as NH ₃ ALLOW pH mark by ECF ONLY if $2.51 \times 10^{-5} \times 0.125$ used AND pH <7 Common errors (Must be to 2 DP) pH = $5.50 \rightarrow 1$ mark (No square root) [H ⁺] = 6.26×10^{-4} from $\sqrt{(2.51 \times 10^{-5})} \times 0.125$ pH = $3.20 \rightarrow 1$ mark [H ⁺] = 8.87×10^{-6} from $\sqrt{(0.125)} \times 2.51 \times 10^{-5}$ pH = $5.05 \rightarrow 1$ mark
(ii)	 Correct equation ✓ Correct acid–base pair labels for correct equation ✓ HN₃ + H₂O ⇒ N₃⁻ + H₃O⁺ ✓ A1 B2 B1 A2 ✓ OR A2 B1 B2 A1 	2	AO1.2 ×2	ALLOW 1 mark for one correct acid–base pair WITH correct labels e.g. H ₂ O H ₃ O ⁺ WITH B1 A1 OR B2 A2

Question	Answer	Marks	AO element	Guidance
(iii)	Structure of 2-methylbutanoic acid ✓ Structure of organic product (primary amine) ✓	3	AO3.2 ×2	ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non-ambiguous
	CO ₂ AND N ₂ as products \checkmark HN ₃ + \bigcirc OH \longrightarrow \rightarrow NH ₂ + CO ₂ + N ₂		AO2.6	Common error With NH ₃ , → CO ₂ + H ₂ ALLOW ECF for equation using a different amine isomer of the organic product e.g. (CH ₃) ₂ CHCH ₂ NH ₂ DO NOT ALLOW ECF from unbranched
				species, e.g. CH ₃ CH ₂ CH ₂ NH ₂ IGNORE HN ₃ in equation, even if missing IGNORE poor connectivity to all groups

Question	Answer	Marks	AO element	Guidance
(c)*	Please refer to the marking instructions on page 6 of this mark scheme for guidance on how to mark this question. Level 3 (5–6 marks) Reaches a comprehensive conclusion to determine the correct formulae of almost all of E, F, G, H, I and J There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated. Level 2 (3–4 marks) Reaches a sound conclusion to determine the correct formulae of at least half of E, F, G, H, I and J There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. Level 1 (1–2 marks) Reaches a simple conclusion to determine the correct formulae of some of E, F, G, H, I and J There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. O marks No response or no response worthy of credit.	9	AO3.1 ×2 AO3.2 ×4	Indicative scientific points may include: Identify of E, F, G, H, I and J • E Cu/copper • F: H ₂ O/water • G: N ₂ /nitrogen • H: CH ₃ COCI OR CICH ₂ CHO OR C ₂ H ₃ OCI • I: CH ₃ CONH ₂ OR H ₂ NCH ₂ CHO • J: NH ₄ Cl/ammonium chloride Examples of reasoning Working $n(\text{CuO}) = \frac{4.77}{(63.5 + 16)} = 0.06 \text{ (mol)}$ $M(\text{E}) = 3.81 \div 0.06 = 63.5$ $n(\text{G}) = \frac{480}{24000} = 0.02$ $M(\text{G}) = \frac{0.560}{0.02} = 28 \text{ (g mol}^{-1})$ Infrared spectrum I contains • C=O (~1700 cm ⁻¹) • NH ₂ (~3200-3400 cm ⁻¹) Equations $3\text{CuO} + 2\text{NH}_3 \rightarrow 3\text{Cu} + 3\text{H}_2\text{O} + \text{N}_2$ CH ₃ COCI + 2NH ₃ \rightarrow CH ₃ CONH ₂ + NH ₄ CI OR CICH ₂ CHO + 2NH ₃ \rightarrow H ₂ NCH ₂ CHO + NH ₄ CI

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