1) a) one point

[delta]S < 0 b/c he number of moles of gaseous products is less than the number of moles of gaseous reactant OR a liquid is formed from gaseous reactants.

b) one point

[delta]G < 0 because [delta]G becomes less negative as the temperature is increased since [delta]S < 0 and [delta]G = [delta]H - T[delta]S. The term - T[delta]S adds a positive number to [delta]H.

c) one point

[delta]H < 0 because the bond energy of the reactants is less than the bond energy of the products.

d) one point

The reaction has a high activation energy OR is kinetically slow, OR a specific neuton of the needs for a catalyst or spark.

2) (a) two points; one for line of answer
- 232.7 J/K = S° (C_2H_6) - (261.4 + 200.9) J./K S° (C_2H_6) = 229.6 J/K
units ignored; 1 point earned for 98.9 J/K; 1 point lost if stoichiometry is not implied in process
(b) three points total; one point each portion; any value for T (e.g., 273 K or 298 K) is allowable:
[delta]H° = (- 84.7 kJ) - (226.7 kJ) = -311.4kJ
= - 311.4kJ - (298 K) (- 0.2327kJ/K) = - 311.4 kJ + 69.3 kJ = - 242.1 kJ
Negative [delta]G° therefore reaction is spontaneous, or Keq > 1 therefore reaction is spontaneous, or products are favored at equilibrium.
(c) two points
ln K = 242.1 ÷ [(8.31 x 10-3) (298)] = 97.7
K = 3 x 1042 (1,2,or 3 significant figures acceptable)
(d) two points; first point earned for correct substitution and correct number of bonds, second point earned for setting equal to [delta]Hrxn and correct calculation of answer; no points earned for "extrapolation" techniques to find carbon-carbon triple bond energy; E* is the energy of the carbon-carbon triple bond.
- 311.4 kJ = [(2) (436) + E* + (2) (414)] - [(347) + (6) (414)]
E* = 820 kJ

3(a) 2.000g x (1 mol / 94.113 g) = 0.02125 mol phenol (one point)
Heat released per mole = 64.98kJ / 0.02125mol = 3,058 kJ/mol (one point)

or, ΔH_{comb} = - 3,058 kJ/mol Units not necessary

(b) ΔH_{comb} = - 3,058 kJ/mol (one point)

- 3,058 kJ = [6 (-395.5) + 3 (-285.85)] - [ΔH°_f phenol] (one point)

ΔH°_f phenol = - 161 kJ (one point)

One point: correct sign of ΔH_{comb}, one point: correct use of moles/coefficients, one point: right substitution

(c)ΔS° = [3 (69.91) + 6 (213.6)] - [7 (205.0) + 144.0 = - 87.67 J/K (one point)

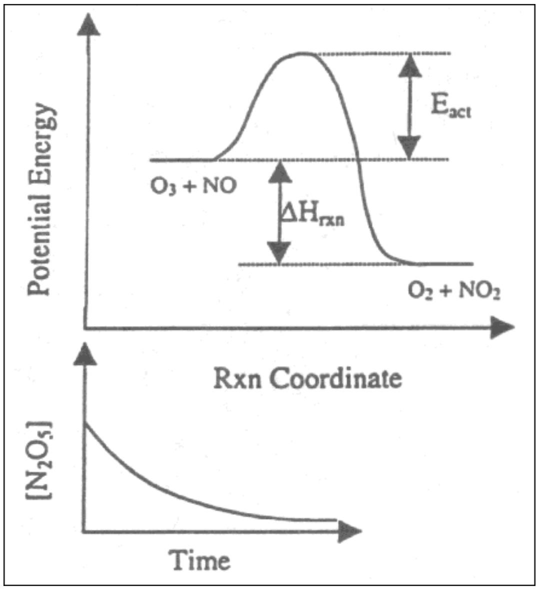
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ = 3,058 kJ - (298 K) (-0.08767 kJ/K) = -3,032 kJ (one point)

Units not necessary; no penalty if correct except for wrong ΔH_{comb} from part (a)

(d) moles gas = 9 x [moles from part (a)] = 9 (0.02125 mol0 = 0.1913 moles gas (one point)

P = (nRT) / V = [(0.193 mol) (0.0821 L atm $mol^{-1}K^{-1}$) (383 K)] / 10.0 L = 0.601 atm (one point)

Units necessary; no penalty for using Celsius temperature if also lost point in part (c) for same error



1) (a) Response must clearly indicate (and distinguish between) Eact and ΔHrxn on graph

Each earns one point

(b) i. Response shows a softly curving line that approaches the time axis and whose slope changes continually.

No penalty if curve crosses time axis or levels out above time axis. Curve must drop initially and continually. No credit earned if [N2O5] increases

ii. Reaction rate is the **slope** of the line **tangent** to any point on the curve. (one point)

Rate must be tied somehow to slope of the graph
Answer may be indicated directly on the graph
Instantaneous rate ust be indicated rather than the average rate

iii. Since "rate = slope = k[N2O5]", the value of k can be determined algebraicallly from the slope at a known value of [N2O5]. (one point)

No penalty for "rate = 2k [N2O5] as a reaction stoichiometry could suggest this answer.
Point can be earned for rate constant = slope of graph if ln[N2O5] vs. time since reaction is first order.
Use half-life or integrated rate law to solve for k can be accepted.

iv. The value of the rate constant is independent of the reactant concentrations, so adding more reactant will not affect the value of k. (one point)

no point earned for simply stating that value of k will not change.
Response must distinguish between rate and rate constant.

(c) i. Rate = k[A] or ln([A]/[A]o) = kt. Since graph of ln[A] vs. time is linear, it must be a first-order reaction. (one point)

Either from of the rate law is acceptable, and both the equation and the brief justification are required to earn the point.
No point earned if response indicates first order because the first graph is not linear.

ii. Determine the slope of the second graph and set "k = -slope." (one point)

Response must indicate both the negative sign and the slope.

2) (a) three points

$1.3 \times 10^{-3} / 4.3 \times 10^{-4} = k\ (0.75)^x\ (0.75)^y / k\ (0.25)^x\ (0.75)^y$ leads to $3 = (3)^x$ leads to $x = 1$, first order in A

$5.3 \times 10^{-3} / 1.3 \times 10^{-4} = k(1.50)(1.50)^y / k(0.75)(0.75)^y \Rightarrow 4 = 2(2)^y \Rightarrow y=1 \Rightarrow$ First order in B

Notes; Verbal descriptions accepted, but no point earned for just "if A doubles, the rate doubles". If A given as second order, 2 points can be earned for showing that B must be zero order.

(b) two points rate = k[A][B] (equation must be consistent with part (a))

k= 4.3×10^{-4}M min^{-1} / (0.25M) (0.75M) = 2.3×10^{-3} M^{-1} min^{-1}

Note; Units must be correct to earn second point. If no part (a) shown, 1 point can be earned for a reasonable (first or second order) rate law.

(c) one point : $\Delta[A] / \Delta t = -2\ (5.3 \times 10^{-3}\ M^{-1}\ \text{min}^{-1}) = -\ 1.06 \times 10^{-2}\ M^{-1}\ \text{min}^{-1}$

Note; Units ignored; no penalty for (⁻) sign.

(d) one point

$8.0 \times 10^{-3}\ M^{-1}\ \text{min}^{-1} = (2.3 \times 10^{-2}\ M^{-1}\ \text{min}^{-1})\ (1.75\ M)\ [B]$ [B] = 2.0 M

Note; No penalty if answer is consistent with wrong part (b).

(e) two points

Mechanism 2 is consistent

rate proportional to [M][A] and [M] proportional to [B] => rate proportional to [A][B]

Notes; Verbal discussion accepted for second point. Mechanism must be consistent with rate law in part (b). Showing that mechanisms 1 and 3 are inconsistent is not required.

3) a) three points (point for each order must include justification)

From exps. 1 and 2: doubling [H_2] while keeping [NO] constant doubles the rate, therefore the reaction is first order in [H_2].

From exps. 3 and 4; doubling [NO] while keeping [H_2] constant quadruples the rate, therefore the reaction is second order in [NO].

Rate = k [H_2] $[NO]^2$

Note: full credit is earned for the rate expression as long as it is consistent with orders described by student.

b) two points (one for value and one for units)

k= Rate / ([H_2] $[NO]^2$)

From exp. 1: $k = 1.8 \times 10^{-4}$ M/min / $[(1.0 \times 10^{-3}\ M)\ (6.0 \times 10^{-3}\ M)^2] = 5.0 \times 10^{3}\ M^{-2}\ \text{min}^{-1}$

Note: the unit is often written as $L^2\ \text{mol}^{-2}\ \text{min}^{-1}$

c) one point

Stoichiometry: NO : H_2 is 1:1

When 0.0010 mole of H_2 had reacted , it must have reacted with 0.0010 mole NO; thus [NO] remaining = 0.0060 - 0.0010 = 0.0050 M

d) three points

(i)For I : $K_{eq} = [N_2O_2] / [NO]^2$ For II: Rate= k[H_2] [N_2O_2] $[N_2O_2] = K_{eq}\ [NO]^2$

Rate = k' [H_2]$[NO]^2$

Note: there must be some clear algebraic manipulation showing that $[N_2O_2]$ is proportional (NOT equal) to $[NO]^2$. Step II is the rate determining step.

(ii) I: $NO + NO \text{--->} N_2O_2$

II: $N_2O_2 + H_2 \text{--->} H_2O + N_2O$

III: $N_2O + H_2 \text{--->} N_2 + H_2O$

I + II + III: $2NO + 2H_2 \text{--->} N_2 + 2\,H_2O$

1) (a) two points The sign of the cell potential will be positive

because (any one is sufficient):

K is greater than 1
the reaction is spontaneous (occurs)
E° for Sr^{2+} is more positive
Standard reduction potential for Sr more negative
E° = + 0.52 V

Note: only 1 point earned for just E° positive because K_{eq} positive.

(b) one point: The oxidizing agent is Mg^{2+}

(c) two points The cell potential would increase

Since all ions are at 1 M, Q for the system is 1 and E° = (RT/nF) ln K so as T increases, so should E°

Note: no credit lost if student recognizes K_{eq} dependence on T. For temperature change in this problem, decrease in ln K term is small relative to the term RT/nF

OR

No change, because in the Nernst equation $E_{cell} = E° - (RT/nF) \ln Q$

$\ln Q = 0$, and $E_{cell} = E°$ Note: this second approach earns 1 point only

(d) two points

E_{cell} will increase

In the equation $E_{cell} = E° - (0.0592 / n) \log Q$

Q = 0.1 therefore log Q is negative therefore term after E° is positive therefore E_{cell} increases

OR

with the concentration of Mg^{2+} larger than that of Sr^{2+}, Le Chatelier's principle predicts the reaction will have a larger driving force to the right and a more positive E_{cell}

(e) one point At equilibrium, $E_{cell} = 0$

Note: "balanced", "neutral", or "no net reaction" not accepted

2) a) 5 points

$M \text{--->} M^{2+} + 2e^-$, for this reaction E° = x $Cu^{2+} + 2e^- \text{--->} Cu$, for this reaction E° = 0.34 volt

0.740 v = x + 0.34 v (summation $E°_{cell}$)

x = 0.40 volt (oxidation potential) - x = - 0.40 volt (for reduction)

b) 7 points

$M + Cu^{2+} \text{--->} M^{2+} + Cu$

Standard state, original concentrations = 1.00 M

At point of discharge $[M^{2+}] = 1.80$ M (correct stoichiometry)

$E = E° - (0.0592 / n) \log Q$: (recognition of Q)

$E = 0.740 - (0.0592 / 2) \log (1.80 / 0.20)$ (substitution) = 0.712 volt

c) 3 points

E = 0 at equilibrium

$E° = (0.0592 / 2) \log ([M^{2+}] / [Cu^{2+}])$

$\log [M^{2+}] / [Cu^{2+}] = [2(0.740) / 0.0592] = 25.0 = \log K$

$K = 1 \times 10^{25}$

3) a) 2 points: $Cu^{2+} + 2 e^- \text{--->} Cu$

b) 2 points: $2 H_2O \text{--->} O_2 + 4 H^+ + 4 e^-$

c) 1 point: any reasonable sketch with correct labels

d) 3 points (1 point each)

measure mass of cathode before and after experiment. measure current, measure time

(Also acceptable: measure volume of O_2, temperature, pressure, current, time.)

4)a) three points

1.100 hr x (3600 sec / hr) = 3960 sec

3960 sec x (0.125 coulomb / sec) = 495 coulombs

495 coulombs x (1 faraday / 96500 coulombs) = 5.13×10^{-3} F

b) one point: $Fe^{3+} + e^- \text{--->} Fe^{2+}$

c) two points

$MnO_4^- + 8 H^+ + 5 e^- \text{--->} Mn^{2+} + 4 H_2O$

$5(Fe^{2+} \text{--->} Fe^{3+} + e^-)$

Sum of the above two half reactions: $MnO_4^- + 8 H^+ + 5 Fe^{2+} \text{--->} Mn^{2+} + 4 H_2O + 5 Fe^{3+}$

d) three points

5.13×10^{-3} faraday x (1 mole Fe^{2+} / 1 faraday) = 5.13×10^{-3} mole Fe^{2+}

5.13×10^{-3} mole Fe x (1 mole MnO_4^- / 5 mole Fe2+) = 1.03×10^{-3} mole MnO_4^-

1.03×10^{-3} mole $MnO_4^- \div 0.02465$ liter = 0.0416 M MnO_4^- (or $KMnO_4$)

Notes related to (a) and (d)

1) In (a) and (d), full credit for calculations on one line
2) in (d), stoichiometric ratio from the equation in (c) received one point
3) In (d), molarity of MnO_4^- based on a candidate's solution received one point