UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2006/2007

October – November 2006

EKC 336E – Chemical Reaction Engineering
[Kejuruteraan Tindakbalas Kimia]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains TEN printed pages and TWO printed pages of Appendix before you begin the examination.

[Sila pastikan bahawa kertas peperiksaan ini mengandungi SEPULUH muka surat yang bercetak dan DUA muka surat Lampiran sebelum anda memulakan peperiksaan ini.]

Instruction: Answer **FOUR (4)** questions.

*[**Arahan:** Jawab **EMPAT (4)** soalan.]*

[Pelajar dibenarkan menjawab semua soalan dalam Bahasa Inggeris ATAU Bahasa Malaysia ATAU kombinasi kedua-duanya.]

...2/-

1. [a] The gas phase reaction of methane to produce carbon and hydrogen:

$$CH_4 \rightarrow 2H_2 + C$$

is carried out isothermally in a continuous plug flow reactor at molar flow rate of methane is 25 mol/h. Calculate the volume necessary to consume 40% of CH_4, assuming that the reaction rate is second order reaction with reaction rate constant of 0.2 dm^3/mol.h. The entering volumetric flow rate is 20 dm^3/h.

[10 marks]

[b] Construct a stoichiometric table in terms of partial pressure (Pi) for the gas phase decomposition of Nitrosyl Chloride (NOCl) to Nitric Oxide (NO) and Chlorine (Cl_2) in a constant volume batch reactor based on the following initial conditions:

$P_{NOCl_1,O} = 0.5$ bar

$P_{Cl_2,O} = 0.1$ bar

(Inert) $P_{N_2,o} = 0.4$ bar

[7 marks]

[c] If the reaction proceeds to 50% completion at constant temperature, what is the total pressure (P) in the vessel?

[5 marks]

[d] If the temperature changes as the reaction proceeds, can the table be constructed in terms of moles? Molar concentrations? Partial pressures? Explain.

[3 marks]

1. [a] Tindakbalas fasa gas metana untuk menghasilkan karbon dan hidrogen:

$$CH_4 \rightarrow 2H_2 + C$$

dijalankan secara sesuhu di dalam reaktor aliran palam berterusan pada kadar aliran molar metana pada 25 mol/jam. Kirakan isipadu yang diperlukan untuk menggunakan 40% CH_4 dengan menganggapkan kadar tindakbalas adalah tertib keudara dengan pemalar kadar tindakbalas 0.2 dm^3/mol.jam. Kadar aliran isipadu suapan adalah 20 dm^3/jam.

[10 markah]

[b] Bina satu jadual stoikiometri menggunakan tekanan separa (Pi) untuk fasa gas penguraian Nitrosil Klorida (NOCl) kepada Nitrik Oksida (NO) dan klorin (Cl_2) di dalam reaktor berkelompok berisipadu malar berdasarkan keadaan awal yang berikut:

$P_{NOCl_1,O} = 0.5$ *bar*

$P_{Cl_2,O} = 0.1$ *bar*

(Lengai) $P_{N_2,o} = 0.4$ *bar*

[7 markah]

[c] Jika tindakbalas adalah 50% lengkap pada suhu malar, apakah jumlah tekanan (P) dalam reaktor?

[5 markah]

[d] Jika suhu berubah sepanjang tindakbalas, bolehkah jadual dibina dalam sebutan mol? Kepekatan molar? Tekanan separa? Terangkan.

[3 markah]

2. [a] Calculate the mean residence time (t^-) and space time (Υ) and explain any difference between them for reaction in a CSTR for each of the following cases:

[i] Homogeneous liquid phase reaction, volume of CSTR (V) = 100 L, feed flow rate (v_o) = 10 L min^{-1}.

[ii] Homogeneous gas phase reaction, V = 100 L, U_o = 200 L min^{-1} at 300 K (T_o); the stoichiometry of the reaction $A_{(g)} = B_{(g)} + C_{(g)}$; the reactor outlet temperature (T) = 350 K; the reactor inlet and outlet pressures essentially the same and relatively low; conversion of A is 40%.

[10 marks]

[b] The irreversible reaction:

$$A \rightarrow B$$

is carried out in a batch reactor and the following concentration-time data are obtained:.

T (min)	C_A (mol/dm^3)
0	1.69
5	1.23
10	0.89
15	0.62
20	0.44
25	0.31
30	0.22

Determine the reaction order, α and the specific reaction rate, k?

[15 marks]

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2. *[a]* *Kirakan masa mastautin purata (t̄) dan masa ruang (Ȳ) dan terangkan sebarang perbezaan antaranya bagi tindakbalas di dalam CSTR bagi kes-kes yang berikut:*

[i] *Tindakbalas fasa cecair homogen, isipadu CSTR (V) = 100 L, kadar aliran suapan (v_o) = 10 L min^{-1}.*

[ii] *Tindakbalas fasa gas homogen, V = 100 L, U_o = 200 L min^{-1} pada 300 K (T_o); stoikiometri tindakbalas $A_{(g)} = B_{(g)} + C_{(g)}$; suhu keluaran reaktor (T) = 350 K; tekanan masukan dan keluaran reaktor adalah sama dan secara relatifnya rendah, penukaran A adalah 40%.*

[10 markah]

[b] *Tindakbalas tak-berbalik:*

$$A \rightarrow B$$

dijalankan di dalam reaktor berkelompok dan data kepekatan-masa yang berikut diperolehi

T (min)	*C_A (mol/dm^3)*
0	*1.69*
5	*1.23*
10	*0.89*
15	*0.62*
20	*0.44*
25	*0.31*
30	*0.22*

Tentukan tertib tindakbalas, α dan kadar tindakbalas tentu, k?

[15 markah]

3. [a] What is the activation energy for a reaction if its rate constant is 2.0 x 10^3 s^{-1} at 25°C and 4.8 x 10^3 s^{-1} at 75°C?

[5 marks]

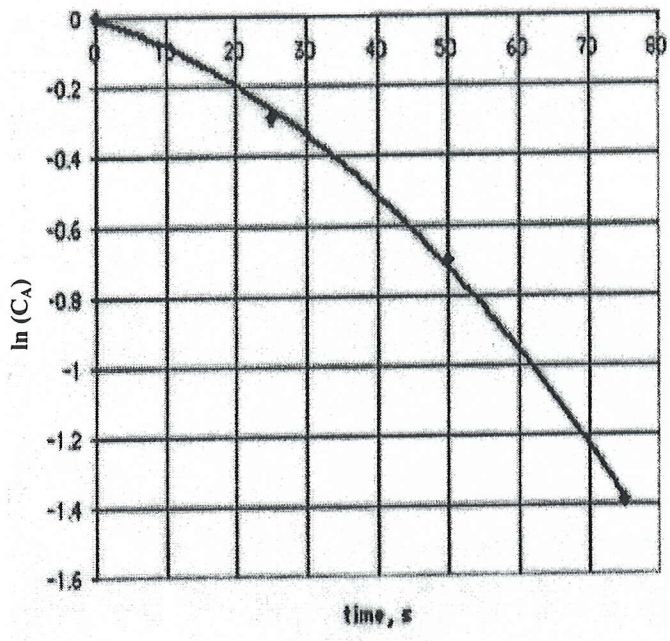
[b] The graphs shown in Figure Q. 3 [b] were prepared from data collected during a single reaction of the type A → B + C at 25°C. Use information from the graphs to answer the following questions. Assume that the unit of the concentration of A, C_A is molarity, M. The x-axis on all three graphs is "time". The y-axes from (a) to (c), are ln C_A, C_A and $1/C_A$.

[i] What is the rate law for this reaction (is it zero-, first-, or second-order in C_A)

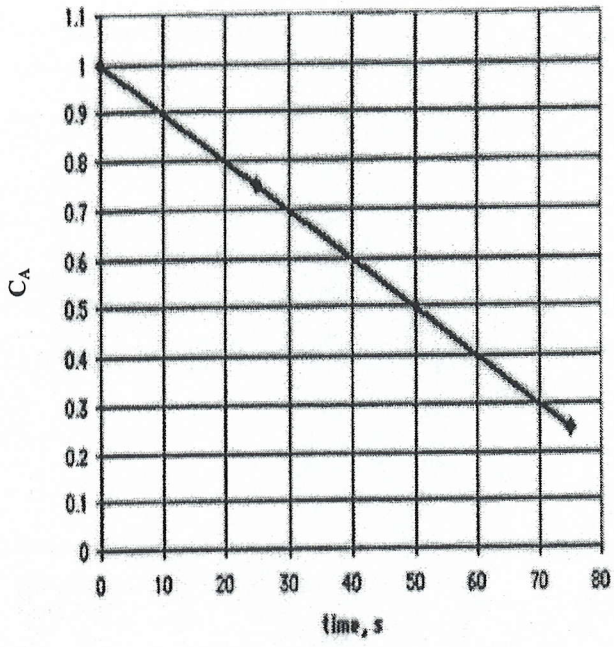
[ii] What is the value of the specific rate constant, k, at 25°C to two significant digits?

[iii] What is the half-life for this reaction at 25°C?

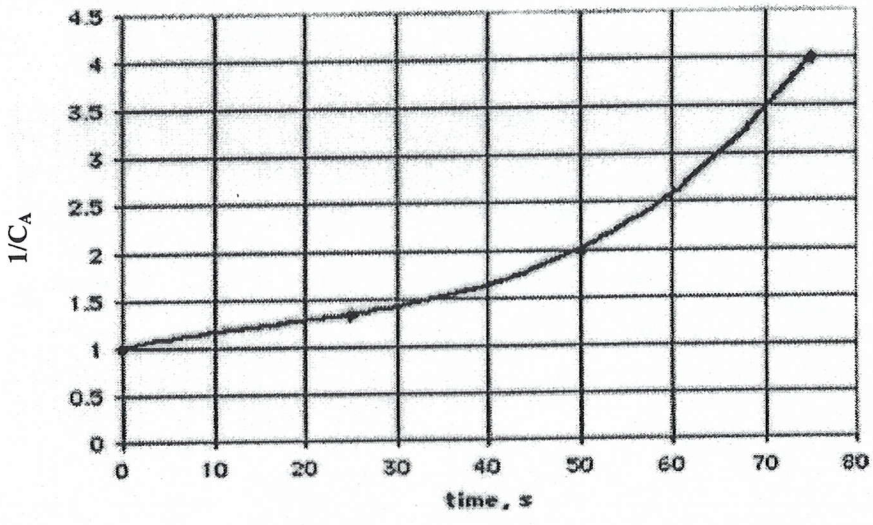
[7 marks]



(a)



(b)



(c)

Figure Q. 3 [b]

[c] The following liquid-phase reactions were carried out in a CSTR at 325 K.

$3A \rightarrow B + C$ $\quad -r_{1A} = k_{1A}C_A$ $\quad k_{1A} = 0.7\ \text{min}^{-1}$

$2C + A \rightarrow 3D$ $\quad r_{2D} = k_{2D}\,C_C^2 C_A$ $\quad k_{2D} = 0.3\ \dfrac{\text{dm}^6}{\text{mol}^2 \cdot \text{min}}$

$4D + 3C \rightarrow 3E$ $\quad r_{3E} = k_{3E}C_D C_C$ $\quad k_{3E} = 0.2\ \dfrac{\text{dm}^3}{\text{mol}^2 \cdot \text{min}}$

...6/-

3-6

The concentrations measured inside the, reactor were $C_A = 0.10$, $C_B = 0.93$, $C_C = 0.51$ and $C_D = 0.049$ all in mol/dm^3.

[i] What are r_{1A}, r_{2A} and r_{3A}?

[ii] What are r_{1B}, r_{2B} and r_{3B}?

[iii] What are r_{1C}, r_{2C} and r_{3C}?

[iv] What are r_{1D}, r_{2D} and r_{3D}?

[v] What are r_{1E}, r_{2E} and r_{3E}?

[13 marks]

3. *[a] Apakah tenaga pengaktifan bagi satu tindakbalas jika pemalar kadar adalah 2.0 x 10^3 s^{-1} pada suhu 25°C dan 4.8 x 10^3 s^{-1} pada suhu 75°C?*

[5 markah]

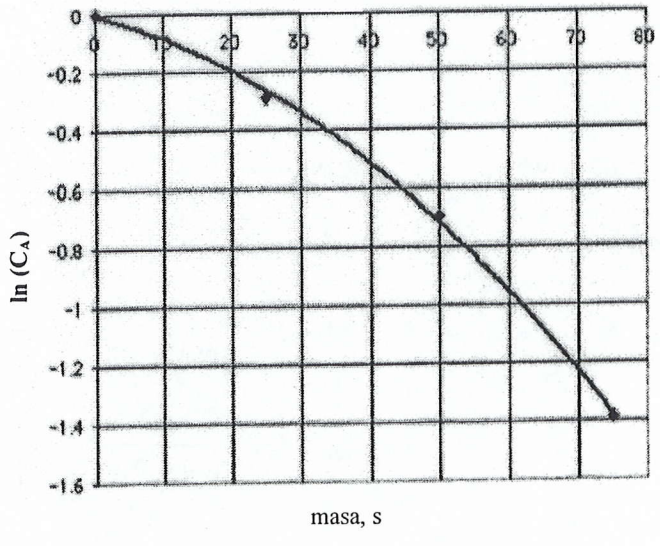
[b] Graf ditunjukkan dalam Rajah S.3[b] disediakan dari data yang dikumpulkan ketika tindakbalas tunggal jenis A → B + C pada suhu 25°C. Gunakan maklumat dari graf untuk menjawab soalan berikut. Anggap unit kepekatan A, C_A adalah kemolaran, M. Paksi x di atas ketiga-tiga graf adalah masa. Paksi y dari (a) hingga (c) adalah ln C_A, C_A and $1/C_A$.

[i] Apakah hukum kadar tindakbalas ini (adakah tertib sifar, pertama atau kedua dalam C_A)

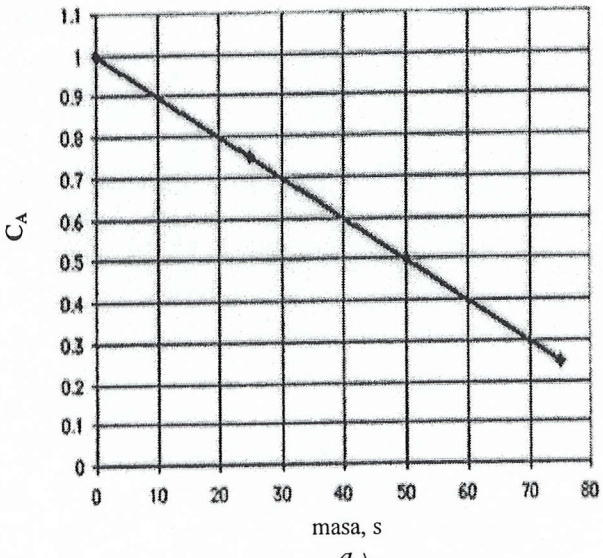
[ii] Apakah nilai pemalar kadar tentu, k, pada suhu 25°C kepada dua angka bererti?

[iii] Apakah separuh hayat bagi tindakbalas ini pada 25°C?

[7 markah]



(a)



(b)

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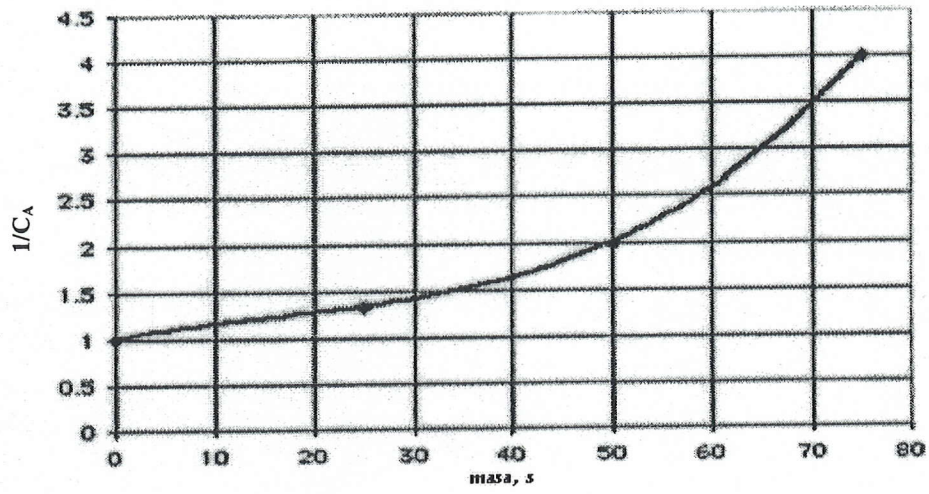

(c)

Rajah S. 3 [b]

[c] *Tindakbalas fasa cecair yang berikut di jalankan di dalam suatu CSTR pada 325 K.*

$3A \rightarrow B + C$	$-r_{1A} = k_{1A}C_A$	$k_{1A} = 0.7\ min^{-1}$
$2C + A \rightarrow 3D$	$r_{2D} = k_{2D}\, C_C^2 C_A$	$k_{2D} = 0.3\ \frac{dm^6}{mol^2 \cdot min}$
$4D + 3C \rightarrow 3E$	$r_{3E} = k_{3E}C_D C_C$	$k_{3E} = 0.2\ \frac{dm^3}{mol^2 \cdot min}$

Kepekatan-kepekatan berikut yang diukur di dalam reaktor adalah $C_A = 0.10$, $C_B = 0.93$, $C_C = 0.51$ dan $C_D = 0.049$ dan semua unit kepekatan adalah dalam mol/dm^3.

[i] *Apakah nilai r_{1A}, r_{2A} dan r_{3A}?*

[ii] *Apakah nilai r_{1B}, r_{2B} dan r_{3B}?*

[iii] *Apakah nilai r_{1C}, r_{2C} dan r_{3C}?*

[iv] *Apakah nilai r_{1D}, r_{2D} dan r_{3D}?*

[v] *Apakah nilai r_{1E}, r_{2E} dan r_{3E}?*

[13 markah]

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4. [a] The thermal decomposition of nitrogen pentoxide to oxygen and nitrogen dioxide

$$2N_2O_5 \rightarrow O_2 + 4NO_2 \qquad \text{(A)}$$

is a gas phase, first-order reaction. The reaction has been studied by a number of investigators, and the following mechanism is the one that appears to give the best agreement with the available experimental facts.

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3 \qquad \text{(B)}$$

$$NO_3 + NO_2 \xrightarrow{k_3} NO + O_2 + NO_2 \qquad \text{(slow) (C)}$$

$$NO + NO_3 \xrightarrow{k_4} 2NO_2 \qquad \text{(D)}$$

In reaction C the NO_2 itself does not react but plays the role of a collision partner that may effect the decomposition of the NO_3 molecule. The NO_2 and NO_3 molecules may react via the two paths indicated by the rate constant k_2 and k_3. The first of these reactions is believed to have a very small activation energy; the second reaction is endothermic and consequently will have an appreciable activation energy. On the basis of this reasoning, it is postulated that k_3 is much less than k_2 and that reaction C is the rate controlling step in the decomposition. Reaction D, which we have included, differs from the final step reported in the literature. Derive an expression for the overall reaction rate based on the above mechanism.

[12 marks]

[b] The concentration readings in Table Q. 4. [b] represent a continuous response to a pulse input into a closed vessel which is to be used as a chemical reactor. Calculate the mean residence time, t of fluid in the vessel and tabulate and plot the exit age distribution E.

Table Q. 4. [b]

Time t, minute	Tracer Output Concentration, C_{pulse} gm/liter fluid
0	0
5	3
10	5
15	5
20	4
25	2
30	1
35	0

[12 marks]

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4. [a] *Penguraian terma bagi nitrogen pentoksida kepada oksigen dan nitrogen dioksida*

$$2N_2O_5 \rightarrow O_2 + 4NO_2 \qquad (A)$$

adalah tindakbalas tertib pertama fasa gas. Tindakbalas tersebut telah dikaji oleh beberapa penyelidik, dan mekanisma berikut didapati sesuai dengan data diperolehi.

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3 \qquad (B)$$

$$NO_3 + NO_2 \xrightarrow{k_3} NO + O_2 + NO_2 \qquad \text{(perlahan) (C)}$$

$$NO + NO_3 \xrightarrow{k_4} 2NO_2 \qquad (D)$$

Dalam tindakbalas C, NO_2 sendiri didapati tidak bertindakbalas tetapi memainkan peranan sebagai rakan pelanggaran yang memberi kesan kepada penguraian molekul NO_3. Molekul-molekul NO_2 dan NO_3 mungkin bertindakbalas melalui dua laluan seperti yang diberikan kadar malar k_2 dan k_3. Tindakbalas pertama didapati mempunyai tenaga pengaktifan yang sangat kecil. Tindakbalas yang kedua adalah endotermik dan oleh itu mempunyai tenaga pengaktifan yang agak tinggi. Berdasarkan fakta ini, dianggarkan k_3 jauh lebih kecil dari k_2 dan tindakbalas C adalah langkah mengawal kadar di dalam penguraian. Tindakbalas D adalah berbeza dari apa yang dilaporkan sebelum dari ini. Terbitkan persamaan untuk kadar tindakbalas keseluruhan untuk mekanisma di atas.

[12 markah]

[b] *Bacaan kepekatan seperti dalam Jadual S.4.[b] menunjukkan respon berterusan terhadap input denyut ke dalam bekas tertutup yang digunakan sebagai reaktor kimia. Kirakan masa maustatin purata (t) cecair di dalam bekas tersebut, jadualkan dan plotkan taburan umur keluaran E.*

Jadual S. 4. [b]

Masa, t, minit	*Kepekatan Pengesan Keluar, C_{denyut} gm/liter cecair*
0	*0*
5	*3*
10	*5*
15	*5*
20	*4*
25	*2*
30	*1*
35	*0*

[12 markah]

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5. [a] There are various types of multiple reactions. Briefly discuss each of them.

[6 marks]

[b] In most instance, it is not possible to eliminate the concentration of the active intermediate in proposing a pseudo-steady state hypothesis (PSSH) in determining the rate law for nonelementry reaction. What are the conditions lead to PSSH approximation?

[6 marks]

[c] The elementary irreversible organic liquid-phase reaction

$$A + B \rightarrow C$$

is carried out adiabatically in a flow reactor. An equal molar feed in A and B enters at 27°C, and the volumetric flow rate is 2 dm^3/s.

[i] Calculate the PFR and CSTR volumes necessary to achieve 85% conversion.

[ii] What is the maximum inlet temperature one could have so that the boiling point of the organic liquid (550 K) would not be exceeded even for complete conversion?

[13 marks]

5. *[a] Terdapat pelbagai jenis tindakbalas berbilang. Bincangkan secara ringkas setiap satu.*

[6 markah]

[b] Dalam kebanyakan kes, adalah sukar untuk menghilangkan kepekatan perantaraan aktif di dalam mengajukan hipotesis keadaan pseudo mantap (PSSH) di dalam menentukan hukum kadar bagi tindakbalas tak asas. Apakah keadaan-keadaan yang membolehkan penganggaran PSSH dilakukan?

[6 markah]

[c] Tindakbalas asas takberbalik organik fasa cecair

$$A + B \rightarrow C$$

Dilakukan secara adiabatik di dalam reaktor aliran. Suapan sama molar A dan B masuk pada suhu 27°C, dan kadar aliran isipadu adalah 2 dm^3/s.

[i] Kirakan isipadu-isipadu PFR dan CSTR yang diperlukan untuk mencapai 85% penukaran.

[ii] Apakah suhu masukan maksima yang boleh dilakukan agar takat didih cecair organik (550 K) tidak akan dijangkau walaupun penukaran lengkap berlaku?

[13 markah]

Lampiran

Useful Integrals in Reactor Design

$$\int_0^x \frac{dx}{1-x} = ln\frac{1}{1-x} \qquad (A-1)$$

$$\int_0^x \frac{dx}{(1-x)^2} = \frac{x}{1-x} \qquad (A-2)$$

$$\int_0^x \frac{dx}{1+\varepsilon x} = \frac{1}{\varepsilon} ln(1+\varepsilon x) \qquad (A-3)$$

$$\int_0^x \frac{1+\varepsilon x}{1-x} dx = (1+\varepsilon) ln\frac{1}{1-x} - \varepsilon x \qquad (A-4)$$

$$\int_0^x \frac{1+\varepsilon x}{(1-x)^2} dx = \frac{(1-\varepsilon)x}{1-x} - \varepsilon ln\frac{1}{1-x} \qquad (A-5)$$

$$\int_0^x \frac{(1+\varepsilon x)^2}{(1-x)^2} dx = 2\varepsilon(1+\varepsilon) ln(1-x) + \varepsilon^2 x + \frac{(1+\varepsilon)^2 x}{1-x} \qquad (A-6)$$

$$\int_0^x \frac{dx}{(1-x)(\Theta_B - x)} = \frac{1}{\Theta_B - 1} ln\frac{\Theta_B - x}{\Theta_B(1-x)} \quad \Theta B \neq 1 \qquad (A-7)$$

$$\int_0^x \frac{dx}{ax^2+bx+c} = \frac{-2}{2ax+b} + \frac{2}{b} \quad for\ b^2 = 4ac \qquad (A-8)$$

$$\int_0^x \frac{dx}{ax^2+bx+c} = \frac{1}{a(p-q)} ln\left(\frac{q}{p}\cdot\frac{x-p}{x-q}\right) \quad for\ b^2 > 4ac \qquad (A-9)$$

$$\int_0^W (1-aW)^{1/2}\, dW = \frac{2}{3a}\left[1-(1-aW)^{3/2}\right] \qquad (A-10)$$

$$\int_0^\infty \left(e^{-kt}\right)\delta(t-\tau)\, dt = e^{-kt} \qquad (A-11)$$

Simpson's five-point formula

$$\int_{x_0}^{x_4} f(x)\, dx = \frac{h}{3}(f_0 + 4f_1 + 2f_2 + 4f_3 + f_4) \qquad h = \frac{X_4 - X_0}{4}$$

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