UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Kedua
Sidang Akademik 1997/98

Februari 1998

EKC 433 : Mangkin Heterogen

Masa: [3 jam]

ARAHAN KEPADA CALON :

Sila pastikan soalan peperiksaan ini mengandungi **ENAM BELAS (16)** mukasurat bercetak dan **SATU (1)** mukasurat lampiran sebelum memulakan peperiksaan.

Kertas soalan ini mengandungi **TUJUH (7)** soalan.

Kertas soalan ini mempunyai **DUA (2)** Bahagian, **BAHAGIAN A** dan **BAHAGIAN B.**

Jawab **LIMA (5)** soalan. Jawab mana-mana **DUA (2)** soalan dari Bahagian A dan **TIGA (3)** soalan dari Bahagian B.

BAHAGIAN A ***PART A***

JAWAB MANA-MANA 2 SOALAN.

ANSWER ANY 2 QUESTIONS.

1. [A] Apakah ciri-ciri penting bahan penyokong mangkin?

(5 markah)

[b] Berikan prosedur untuk menyediakan 0.1% Pt / Al_2O_3 mangkin melalui kaedah pengisitepuan.

(5 markah)

[c] Bincangkan perbezaan antara pengkimierapan dan penjerapan fizikal.

(5 markah)

[d] Terangkan peranan penggalak mangkin dan senaraikan sifat-sifat penggalak tekstural.

(5 markah)

1. [a] What are the important characteristics of a catalyst support?

(5 marks)

[b] Give stepwise procedure for the preparation of 0.1% Pt / Al_2O_3 catalyst by impregnation technique.

(5 marks)

[c] Discuss the difference between chemisorption and physical adsorption.

(5 marks)

[d] Describe the role of catalyst promoters in catalyst formulation and list the properties of a textural promoter.

(5 marks)

2. Seorang perekabentuk loji industri yang baru mahu menggunakan satu mangkin bernama-kod CR di dalam satu langkah yang melibatkan pemfluorinan butadiena. Sebagai langkah pertama penyelidikan ini, mereka perlu menentukan jenis isoterma penjerapan. Isipadu butadiena terjerap per gram CR pada 15°C bergantung kepada tekanan seperti yang diberikan berikut:

P(Torr)	100	200	300	400	500	600
$V_a(cm^3)$	17.9	33.0	47.0	60.8	75.3	91.3

[a] Adakah isoterma Langmuir sesuai pada tekanan ini? Tunjukkan keputusan dengan memplotkan isoterma Langmuir.

(5 markah)

[b] [i] P^o ialah tekanan di atas lapisan tebal makroskopik cecair tulen di atas permukaan. Pada 15°C, P^o (butadiena) = 1500 Torr. Tunjukkan samada isoterma BET memberi gambaran yang lebih baik untuk penjerapan butadiena di atas sampel CR.

(5 markah)

[ii] Tentukan isipadu terjerap untuk membentuk lapisan mono (V_m).

(5 markah)

[iii] Kirakan pemalar BET, C.

(5 markah)

2. *The designer of a new industrial plant wanted to use a catalyst code-name CR in a step involving the fluorination of butadiene. As a first step in the investigation they determined the form of adsorption isotherm. The volume of butadiene adsorbed per gram CR at 15°C depended on the pressure as given below:*

P(Torr)	*100*	*200*	*300*	*400*	*500*	*600*
$V_a(cm^3)$	*17.9*	*33.0*	*47.0*	*60.8*	*75.3*	*91.3*

[a] *Is the Langmuir isotherm suitable at this pressure? Show your result by plotting the Langmuir isotherm.*

(5 marks)

[b] *[i]* P^o *is the pressure above a macroscopically thick layer of the pure liquid on the surface. At 15°C,* P^o *(butadiene) = 1500 Torr. Investigate whether BET isotherm gives a better description of the adsorption of butadiene on CR sample.*

(5 marks)

[ii] *Determine the volume adsorbed to form a monolayer* (V_m).

(5 marks)

[iii] *Calculate the BET constant, C.*

(5 marks)

3. [a] Lakarkan gambarajah skema spektrometer fotoelektron sinar-X dan bincangkan kelebihan spektroskopi fotoelektron sinar-X (XPS) sebagai satu kaedah untuk menganalisa permukaan?

(5 markah)

[b] Spektrum XPS untuk satu sampel yang diliputi emas telah diperolehi dengan menggunakan sinaran aluminium K_α (1487 eV). Tenaga fotoelektron untuk paras $4f_{7/2}$ emas telah disukat pada 1353 eV. Tenaga penambatan untuk unsur-unsur diberikan dalam jadual 1 dalam lampiran.

[i] Apakah tenaga fotoelektron yang patut kamu dapati untuk puncak fotoelektron Karbon 1s.

(3 markah)

[ii] Di dalam spektrum yang sama, satu puncak didapati pada tenaga fotoelektron 1381 eV. Carikan unsur yang bertanggungjawab terhadap puncak itu.

(3 markah)

[iii] Dengan spektrometer yang sama, apakah tenaga fotoelektron untuk puncak Karbon 1s jika sinaran magnesium K_α (1254 eV) digunakan?

(4 markah)

[c] Bincangkan perbezaan antara spektroskopi elektron Auger (AES) dan XPS.

(5 marks)

3. *[a] Draw a schematic diagram of an X-ray photoelectron spectrometer and discuss the advantages of X-ray photoelectron spectroscopy (XPS) as a method for analysis of surface?.*

(5 marks)

[b] The XPS spectrum of a gold coated sample was obtained using aluminium K_α (1487 eV) radiation. The photoelectron energy of the $4f_{7/2}$ level of gold is measured at 1353 eV. The binding energies of selected elements are given in Table 1 in the appendix.

[i] At what photoelectron energy should you look for the carbon 1s photoelectron peak?

(3 marks)

[ii] On the same spectrum, a prominent peak is noted at a photoelectron energy of 1381 eV. Assign the peak to the element responsible.

(3 marks)

[iii] With the same spectrometer, at what photoelectron energy should the carbon 1s peak be if magnesium K_α (1254 eV) radiation were used?

(4 marks)

[c] Discuss the difference between Auger electron spectroscopy(AES) and XPS.

(5 marks)

Bahagian B (Sila jawab dalam Bahasa Inggeris)
PART B

JAWAB MANA-MANA 3 SOALAN
ANSWER ANY 3 QUESTIONS.

4. Fasa wap bagi penghidratan etilena dilakukan di dalam skala komersil reaktor padatan tetap menggunakan pelet mangkin sfera asid fosforik di atas kieselguhr yang mempunyai garispusat d_p. Etilena dan stim (15 mol stim bagi setiap mol etilena) memasuki reaktor pada 150°C.

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

haba tindakbalas adalah tetap: $\Delta H_R(150°C) = -22{,}000$ cal/mol.

Tekanan sistem berkenaan adalah 3 atm dan pada keadaan ini tiada fasa cecair hadir. Juga, tiada tindakbalas berlaku dengan ketiadaan mangkin. Pemindahan jisim luaran (gas pukal kepada permukaan pelet) dan resapan intra-pelet kedua-duanya akan memberi kesan kepada perlakuan reaktor berkenaan. Kadar intrinsik pada tapak mangkin bertertib pertama bagi etilena dan wap-air. Abaikan tindakbalas berbalik.

[a] Terbitkan persamaan tak tersirat bagi pertukaran etilena meninggal reaktor dalam sebutan pemalar pemindahan-jisim, k_m , berdasarkan kepada luas permukaan luar pelet tersebut; faktor keberkesanan η dan keperluan kuantiti-kuantiti yang lain. Andaikan tiada serakan paksi di dalam reaktor tiub, tiada kepekatan kecerunan jejari atau halaju dan keadaan isoterma. Abai susut tekanan (ΔP) melalui lapisan mangkin.

(12 markah)

[b] Dengan menggunakan ungkapan yang diterbitkan di dalam bahagian [a], kirakan pertukaran C_2H_4 di dalam kumbah reaktor bagi keadaan yang berikut.

[1] Resapan berkesan etilena di dalam pelet mangkin pada 150°C dan 3 atm = 1.05 cm^2/s.

[2] Garispusat pelet; d_p = 6 mm

[3] Pemalar pemindahan jisim luaran, k_m = 1.0 cm/s

[4] Pemalar kadar intrinsik bagi tindakbalas tertib kedua pada tapak mangkin, $k_2 = 2.13 \times 10^5$ (cm^6/s. mol. g mangkin)

[5] Ketumpatan pelet mangkin; $\rho_p = 1.5 g/cm^3$ pelet.

[6] Ketumpatan lapisan, $\rho_B = 1.2 g/cm^3$ isipadu reaktor.

[7] Garis pusat reaktor, 2R = 15 cm

[8] Panjang lapisan mangkin = 1.5 meter

[9] Jumlah kadar aliran yang memasuki reaktor pada 150°C dan tekanan 3 atm = 255 dm^3/s.

(8 markah)

Data:

$$\eta = \frac{1}{\phi_s}\left(\frac{1}{\tanh 3\phi_s} - \frac{1}{3\phi_s}\right)$$

where $\phi_s = \frac{r}{2}\sqrt{\frac{k_1 \rho_p}{D_e}}$

4. *The vapour phase hydration of ethylene is being carried out in a commercial scale fixed bed reactor using spherical catalyst pellets phosphoric acid-on-kieselguhr whose diameter is d_p. Ethylene and steam (15 moles of steam per mole ethylene) enter the reactor at 150°C.*

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

The heat of reaction is essentially constant; $\Delta H_R(150°C) = -22,000$ cal/mol.

The system pressure is 3 atm and at these conditions no liquid phase is present. Also no reaction occurs in the absence of catalyst. External mass transfer (bulk-gas-to-pellet-surface) and intrapellet diffusion both can affect the performance of the reactor. The intrinsic rate at a catalyst site is first order in ethylene and first order in water vapour. Neglect the reverse reaction.

[a] *Derive an explicit equation for the conversion of ethylene leaving the reactor in terms of the mass-transfer coefficient, k_m, based upon the outer surface area of the pellet, the effectiveness factor η, and, other quantities as needed. Assume that there is no axial dispersion in the tubular reactor, no radial gradients of concentration or velocity, and assume isothermal conditions. Neglect pressure drop (ΔP) through the catalyst bed.*

(12 marks)

[b] *Using the derived expression in Part A, calculate the conversion of C_2H_4 in the reactor effluent for the following conditions :*

[1] *Effective diffusivity of ethylene in the catalyst pellets at 150°C and 3 atm = $1.05\ cm^2/s$.*

[2] *Pellet diameter, $d_p = 6$ mm*

[3] *External mass transfer coefficient, $k_m = 1.0$ cm/s*

[4] *Intrinsic rate constant for second order reaction at a catalyst site, $k_2 = 2.13 \times 10^5$ (cm^6/s .mol.g of catalyst).*

[5] *Density of catalyst pellets, $\rho_p = 1.5 g/cm^3$ of pellet.*

[6] *Density of bed, $\rho_B = 1.2 g/cm^3$ of reactor volume.*

[7] *Diameter of reactor, 2R = 15 cm.*

[8] *Length of catalyst bed = 1.5 meter.*

[9] *Total volumeteric flow rate entering the reactor, at 150°C and 3 atm pressure = $255\ dm^3/s$.*

(8 marks)

Data:

$$\eta = \frac{1}{\phi_s}\left(\frac{1}{\tanh 3\phi_s} - \frac{1}{3\phi_s}\right)$$

$$\text{where } \phi_s = \frac{r}{2}\sqrt{\frac{k_1\rho_p}{D_e}}$$

5. Penyahidratan fasa wap etanol untuk menghasilkan dietil-eter dan air telah dilakukan di atas mangkin γ-Alumina pada 120°C dengan keputusan yang berikut:

No.	Berat mangkin, W (g)	P_{A_0} (atm)	P_{E_0} (atm)	P_{W_0} (atm)	Kadar tindakbalas $(-r' \times 10^4)$ $\left(\frac{\text{mol}}{\text{g cat. min}}\right)$
1	14.3	1.000	0.00	0.00	1.347
2	14.3	0.947	0.053	0.00	1.335
3	14.3	0.877	0.123	0.00	1.288
4	14.3	0.781	0.219	0.00	1.360
5	14.3	0.471	0.529	0.00	0.868
6	14.3	0.572	0.428	0.00	1.003
7	14.3	0.704	0.296	0.00	1.035
8	14.3	0.641	0.359	0.000	1.068
9	22.6	1.000	0.000	0.000	1.220
10	22.6	0.755	0.000	0.245	0.571
11	22.6	0.552	0.00	0.448	0.241
12	22.6	0.622	0.175	0.203	0.535
13	22.6	0.689	0.00	0.000	1.162

Tindakbalas tersebut diwakilkan sebagai

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

$$A \rightarrow E + W$$

[a] Cadangkan satu mekanisma dan hukum kadar konsisten dengan data eksperimen di atas.

(10 markah)

[b] Nilaikan semua parameter-parameter hukum kadar.

(10 markah)

5. *The vapour phase dehydration of ethanol to give diethyl-ether and water was carried out over a γ-Alumina catalyst at 120°C with the following results :*

No.	*Catalyst Weight, W (g)*	P_{A_0} *(atm)*	P_{E_0} *(atm)*	P_{W_0} *(atm)*	*Rate of reaction,* $(-r' \times 10^4)$ $\left(\frac{\text{mol}}{\text{g cat. min}}\right)$
1	*14.3*	*1.000*	*0.00*	*0.00*	*1.347*
2	*14.3*	*0.947*	*0.053*	*0.00*	*1.335*
3	*14.3*	*0.877*	*0.123*	*0.00*	*1.288*
4	*14.3*	*0.781*	*0.219*	*0.00*	*1.360*
5	*14.3*	*0.471*	*0.529*	*0.00*	*0.868*
6	*14.3*	*0.572*	*0.428*	*0.00*	*1.003*
7	*14.3*	*0.704*	*0.296*	*0.00*	*1.035*
8	*14.3*	*0.641*	*0.359*	*0.000*	*1.068*
9	*22.6*	*1.000*	*0.000*	*0.000*	*1.220*
10	*22.6*	*0.755*	*0.000*	*0.245*	*0.571*
11	*22.6*	*0.552*	*0.00*	*0.448*	*0.241*
12	*22.6*	*0.622*	*0.175*	*0.203*	*0.535*
13	*22.6*	*0.689*	*0.00*	*0.000*	*1.162*

The reaction is represented as:

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

$$A \rightarrow E + W$$

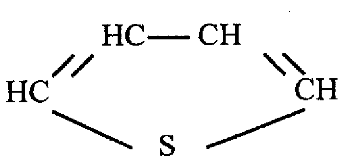
[a] *Suggest a mechanism and rate law consistent with the experimental data.*

(10 marks)

[b] *Evaluate all the rate law parameters.*

(10 marks)

6. Satu minyak hidrokarbon dinyahsulfur sebelum memasuki pemecahan bermangkin. Daripada semua pelbagai sebatian sulfur yang hadir (merkaptan, sulfida, disulfida, dan lain-lain), salah satu sebatian yang paling susah untuk dinyahsulfur ialah tiofena. Dengan mangkin kobalt-molibdenum oksida bersulfur di atas alumina, tiofena (B) bertindakbalas dengan hidrogen untuk menghasilkan butana dan H_2S.



$$+ 4H_2 \rightarrow C_4H_{10} + H_2S$$

Thiophene
B

Satu reaktor lapisan tercucur dibina di atas andaian jika tiofena tahan panas bertindakbalas, sebatian sulfur yang lain juga akan turut terhidrogen.

Hidrogen tulen dan cecair hidrokarbon akan disuap ke bahagian atas lapisan mangkin yang beroperasi pada 200°C dan 40 atm. Abaikan pemeluapan tiofena daripada cecair pada keadaan ini.

[a] Andaikan kadar tindakbalas pada tapak mangkin dan kadar pemindahan jisim daripada cecair kepada zarah-zarah mangkin adalah cukup perlahan supaya cecair tersebut tertepu dengan hidrogen pada keseluruhan turus. Sementara tindakbalas berkenaan bertertib kedua, andaikan kepekatan tiofena tersebut besar berbanding dengan hidrogen yang terlarut didalam minyak. Dengan itu kadar intrinsik akan bertertib pseudo-pertama terhadap hidrogen. Juga, kadar intrinsik adalah cukup perlahan supaya faktor keberkesanan adalah satu. Terbitkan satu ungkapan bagi nisbah penyingkiran (pertukaran) tiofena daripada minyak, dengan mengandaikan cecair berkenaan beraliran palam.

(12 markah)

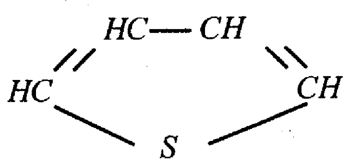
[b] Dengan menggunakan terbitan yang diperolehi di bahagian [a], kirakan kedalaman lapisan mangkin yang diperlukan untuk menyingkirkan 75% tiofena berkenaan. Kepekatan suapan tiofena ialah 1000 ppm. Halaju permukaan cecair ialah 5 cm/s. Pemalar kadar tertib pertama adalah k_{H2} = 0.11 (cm^3/g.s) dan k_B = 0.07 (cm^3/g.s), dan pemalar isipadu pemindahan jisim daripada cecair adalah $(k_c a_c)_{H_2} = 0.50 s^{-1}$ dan $(k_c a_c)_B = 0.3\ s^{-1}$, $\rho_B = 0.96$ g/cm^3.

Pemalar Henry untuk H_2:

$$H_{H2} \text{ at } 200°C = 50 \left(\frac{\text{mol}}{\text{cm}^3\text{gas}}\right) \Bigg/ \left(\frac{\text{mol}}{\text{cm}^3 \text{ in liquid}}\right)$$

$$R = 82.0 \frac{(\text{atm})\ \text{cm}^3}{\text{mol.K}}$$

6. *A hydrocarbon oil is to be desulfurized prior to catalytic cracking. Of the various sulfur compounds present (mercaptans, sulfides, disulfides, etc) one of the most difficult to desulfurize is thiophene. With a sulfided cobalt-molybdenum oxide catalyst on alumina, thiophene (B) reacts with hydrogen to form butane and H_2S.*

 $+ 4H_2 \rightarrow C_4H_{10} + H_2S$

Thiophene
B

A trickle-bed reactor is to be designed on the supposition that if the refractory thiophene is reacted, the other sulfur compounds will also have been hydrogenated.

Pure hydrogen and the hydrocarbon liquid will be fed to the top of the catalyst bed operating at 200°C and 40 atm. Neglect the vapourisation of thiophene from the liquid at these conditions.

[a] *Assume that the reaction rate at the catalyst sites and the mass-transfer rate from liquid to catalyst particles are slow enough that the liquid is saturated with hydrogen throughout the column. While the reaction probably is second order, assume that the thiophene concentration is relatively large with respect to that of hydrogen dissolved in the oil. Then the intrinsic rate will be pseudo-first order in hydrogen. Also, the intrinstic rate is slow enough that the effectiveness factor is unity. Derive an expression for the fractional removal (conversion) of thiophene from the oil, assuming plug flow of liquid.*

(12 marks)

[b] *Using the derivation in part (a), calculate the catalyst bed depth required to remove 75% of the thiophene. The feed concentration of thiophene is 1000 ppm. The superficial liquid velocity will be 5 cm/s. The first-order rate constants are* $k_{H_2} = 0.11\ (cm^3/g.s)$ *and* $k_B = 0.07\ (cm^3/g.s)$*, and the volumetric mass transfer coefficients from liquid to particle are* $(k_c a_c)_{H_2} = 0.50 s^{-1}$ *and* $(k_c\ a_c)_B = 0.3\ s^{-1}$, $\rho_B = 0.96\ g/cm^3$.

Henry's constant of H_2 *:*

$$H_{H_2}\ at\ 200°C = 50\left(\frac{mol}{cm^3 gas}\right)\Big/\left(\frac{mol}{cm^3\ in\ liquid}\right)$$

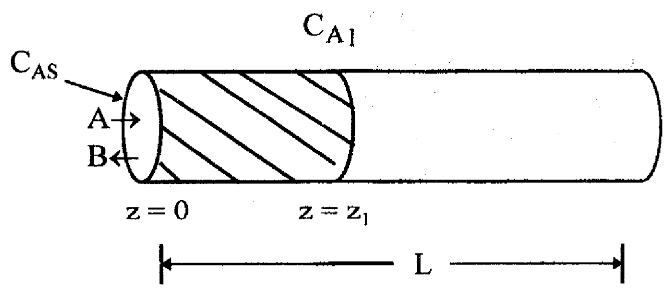
$$R = 82.0\frac{(atm)\ cm^3}{mol.K}$$

(8 marks)

7. Tindakbalas pengisomeran asas

$$A \rightarrow B$$

berlaku di atas dinding liang mangkin berselindar. Dalam ujikaji pertama, satu racun mangkin P memasuki reaktor sekali dengan bahan tindakbalas A. Untuk menganggarkan kesan keracunan, kita andaikan racun membuat dinding liang mangkin dekat dengan mulut liang tidak berkesan sehingga jarak z supaya tiada tindakbalas berlaku pada dinding kawasan kemasukan.



[a] Tunjukkan bahawa sebelum keracunan pada liang berlaku, faktor keberkesanan diberi sebagai

$$\eta = \frac{1}{\phi}\tanh\phi$$

$$\phi = L\sqrt{\frac{2k''}{rD_{AB}}}$$

di mana

k''= pemalar kadar tindakbalas (panjang/masa)

r = jejari liang (panjang)

D_{AB} = resapan berkesan molekul (keluasan/masa).

[b] Terbitkan ungkapan bagi susuk kepekatan dan juga fluk molar bagi A di dalam kawasan tidak berkesan $0 < Z < Z_l$, di dalam sebutan Z_l, D_{AB}, C_A dan C_{AS}. Dengan tidak menyelesaikan seterusnya persamaan perbezaan, tunjukkan faktor keberkesanan yang baru η' bagi liang teracun di beri sebagai:

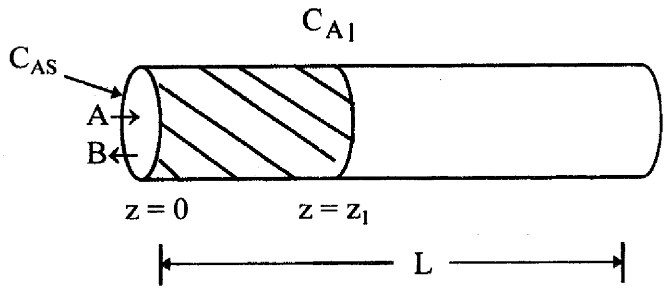
$$\boxed{\eta' = \frac{\tanh\left\{\phi\left(1-\frac{Z}{L}\right)\right\}}{\phi+\phi^2\left(\frac{Z}{L}\right)\tanh\left\{\phi\left(1-\frac{Z}{L}\right)\right\}}}$$

(12 markah)

7. *The elementary isomerization reaction*

$$A \rightarrow B$$

is taking place on walls of a cylinderical catalyst pore. In one run, a catalyst poison P entered the reactor together with the reactant A. To estimate the effect of poisoning, we assume that the poison renders the catalyst pore walls near the pore mouth ineffective up to a distance Z_l, so that no reaction takes place on the walls in this entry region.



[a] *Show that before poisoning of the pore occurred, the effectiveness factor was given by*

$$\eta = \frac{1}{\phi}\tanh\phi$$

$$\phi = L\sqrt{\frac{2k''}{rD_{AB}}}$$

where

k''= *reaction rate constant (length/time)*

r = *pore radius (length)*

D_{AB} = *effective molecular diffusivity (area/ time).*

(8 marks)

[b] *Derive an expression for the concentration profile and also for the molar flux of A in the ineffective region* $0 < Z < Z_1$ *in terms of* Z_1, D_{AB}, C_A *and* C_{AS}. *Without solving any futher differential equations, show that the new effectiveness factor* η' *for the poisoned pore is given as :*

$$\boxed{\eta' = \frac{\tanh\left\{\phi\left(1-\frac{Z}{L}\right)\right\}}{\phi+\phi^2\left(\frac{Z}{L}\right)\tanh\left\{\phi\left(1-\frac{Z}{L}\right)\right\}}}$$

(12 marks)

-oooOooo-

LAMPIRAN 1

Table 1. Selected ESCA Binding Energies

Atomic Number	Element	Binding Energy (E_b),eV	Type of Electron
3	Li	55	1s
4	Be	111	
5	B	188	
6	C	284	
7	N	399	
8	O	532	
9	F	686	
10	Ne	867	1s
11	Na	1072;63	1s;2s
12	Mg	89	2s
13	Al	74;73	$2p_{1/2};2p_{3/2}$
14	Si	100;99	
15	P	136;135	
16	S	165;164	
17	Cl	202;200	
19	K	297;294	
20	Ca	350;347	
21	Sc	407;402	
22	Ti	461;455	
23	V	520;513	
24	Cr	584;575	
25	Mn	652;641	
26	Fe	723;710	
27	Co	794;779	
28	Ni	872;855	
29	Cu	951;931	
30	Zn	1044;1021	$2p_{1/2};2p_{3/2}$
32	Ge	129;122	$3p_{1/2};3p_{3/2}$
47	Ag	373;367	$3d_{3/2};3d_{5/2}$
78	Pt	74;70	$4f_{5/2};4f_{7/2}$
79	Au	87;83	$4f_{5/2};4f_{7/2}$