CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 322: PHYSICAL CHEMISTRY III

STREAMS: BSC. CHEM **TIME: 2 HOURS**

DAY/DATE: FRIDAY 20/12/2024 **2.30 P.M. – 4.30 P.M.**

INSTRUCTIONS:

- **Answer question one and any other two**

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^{8}	$m\ s^{-1}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^{4}	$C\ mol^{-1}$
Boltzmann's constant	k	1.380 65	10^{-23}	$J\ K^{-1}$
Gas constant	$R = N_A k$	8.314 47		$J\ K^{-1}\ mol^{-1}$
		8.314 47	10^{-2}	$dm^3\ bar\ K^{-1}\ mol^{-1}$
		8.205 74	10^{-2}	$dm^3\ atm\ K^{-1}\ mol^{-1}$
		6.236 37	10	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	8.854 19	10^{-12}	$J^{-1}\ C^2\ m^{-1}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$J^{-1}\ C^2\ m^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$J\ s^2\ C^{-2}\ m^{-1}\ (= T^2\ J^{-1}\ m^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	$J\ T^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	$J\ T^{-1}$
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	10^{-8}	$W\ m^{-2}\ K^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 37	10^{5}	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		$m\ s^{-2}$
Gravitational constant	G	6.673	10^{-11}	$N\ m^2\ kg^{-2}$

*Exact value

QUESTION ONE (30 MARKS)

a. (i) For silver, $\overline{C}_p$/(J/K mol) = 23.43 + 0.00628T. Calculate ΔH if 3 mol of silver are raised from 25 °C to the melting point, 961 °C, under 1 atm pressure. (2marks)

(ii) Derive the relationship between C_p and C_v. (2 marks)

(iii) An ideal gas, $\overline{C}_v = \frac{5}{2}R$, is expanded adiabatically against a constant pressure of 1 atm until it doubles in volume. If the initial temperature is 25 °C, and the initial pressure is 5 atm, calculate T_2; then calculate Q, W, ΔU, and ΔH per mole of gas for the transformation.

(2 marks)

(iv) Compute the heat of reaction at 1000 °C = 1273 K for

$$\tfrac{1}{2} H_2 (g) + \tfrac{1}{2} Cl_2 (g) \rightarrow HCI (g)$$

Given $\Delta H^o{}_{298}$ = - 92.312 kJ/mol and the data for Cp from Table 7. 1 (2 Marks)

Table 7.1
Heat capacity of gases as a function of temperature

$\bar{C}_p/R = a + bT + cT^2 + dT^3$

Range: 300 K to 1500 K

	a	$b/10^{-3}\,K^{-1}$	$c/10^{-7}\,K^{-2}$	$d/10^{-9}\,K^{-3}$
H_2	3.4958	− 0.1006	2.419	
O_2	3.0673	+ 1.6371	− 5.118	
Cl_2	3.8122	1.2200	− 4.856	
Br_2	4.2385	0.4901	− 1.789	
N_2	3.2454	0.7108	− 0.406	
CO	3.1916	0.9241	− 1.410	
HCl	3.3876	0.2176	+ 1.860	
HBr	3.3100	0.4805	0.796	
NO	3.5326	− 0.186	12.81	−0.547
CO_2	3.205	+ 5.083	− 17.13	
H_2O	3.633	1.195	+ 1.34	
NH_3	3.114	3.969	− 3.66	
H_2S	3.213	2.870	− 6.09	
SO_2	3.093	6.967	− 45.81	+1.035
CH_4	1.701	9.080	− 21.64	
C_2H_6	1.131	19.224	− 55.60	
C_2H_4	1.424	14.393	− 43.91	
C_2H_2	3.689	6.352	− 19.57	
C_3H_8	1.213	28.782	− 88.23	
C_3H_6	1.637	22.703	− 69.14	
C_3H_4	3.187	15.595	− 47.59	
C_6H_6	−0.206	39.061	−133.00	
$C_6H_5CH_3$	+0.290	47.048	−157.14	
C(graphite)	−0.637	7.049	− 51.99	1.384

Calculated from the compilations of H. M. Spencer and J. L. Justice, *J. Am. Chem. Soc.*, **56**:2311 (1934); H. M. Spencer and G. N. Flanagan, *J. Am. Chem. Soc.*, **64**:2511 (1942); H. M. Spencer, *Ind. Eng. Chem.*, **40**:2152 (1948).

(v) Some texts define work W' as positive when a weight is lowered in the surroundings; that is, When the surroundings do work on the system. How can the first law be expressed in terms of Q andW'? (Justify the sign in front of W'.) (1 mark) b.

(i) One mole of solid gold is raised from 25 °C to 100 °C at constant pressure. $\overline{C}_P$/ (J/K mol) = 23.7 + 0.00519T. Calculate ΔS for the transformation. (1 mark)

(ii) For the reaction

$\frac{1}{2}N_2$ (g) + $\frac{3}{2}H_2$ (g) ⇌ NH_3 (g), the equilibrium constant is 6.59 x 10^{-3} at 450 °C. Compute the standard reaction Gibbs energy at 450 °C. . (1 mark)

(iii) Under standard conditions, 1 g of LiCl powder is dissolved in 50 ml of water (Fig. 4.3).

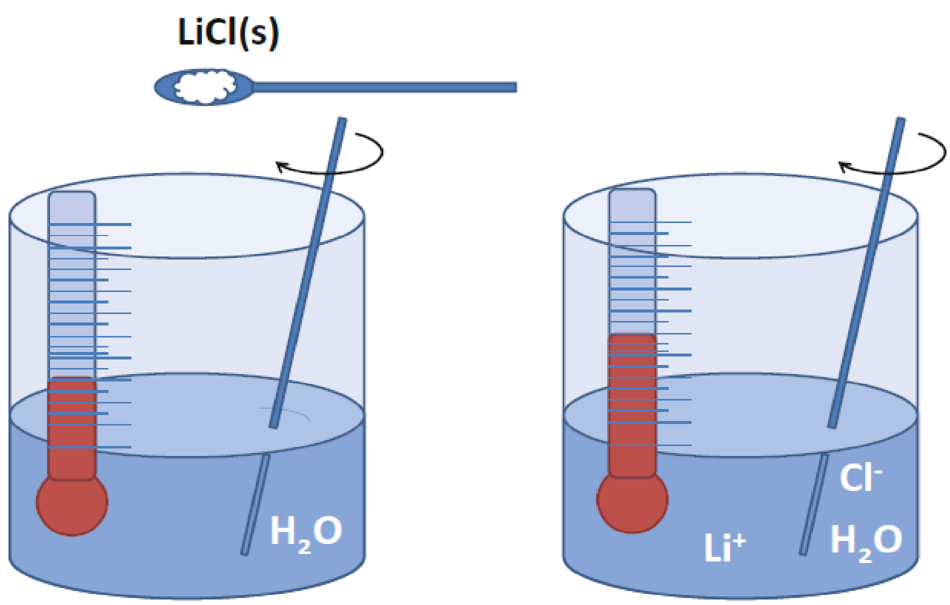

Fig. 4.3 A simple form of calorimetry to measure the heat of solvation of a salt

I. As the solution is stirred, the temperature increases from 298 to 302.2K. The constant pressure molar heat capacity of water is 75.3 JK^{-1} mol^{-1}. Estimate the molar standard heat of solvation of LiCl. You may ignore the contribution of the dissolved LiCl to the heat capacity of the solution. The density of water is 1 gml^{-1}. (2 marks)

II. In another experiment, 1 g KCl(s) is dissolved in the same amount of water under the same conditions. A temperature reduction of 1.1K was measured. Determine the molar standard heat of solvation of KCl and calculate the standard heat of formation of K^+ (aq) relative to

the value of Li^+, if the standard heats of formation for KCl and LiCl are -436.7 and -408.7 $kJmol^{-1}$ respectively. (1 marks)

(iv) Consider a sealed reaction vessel containing graphite (C(s)), nickel oxide (NiO(s)), and noble

gas. The vessel may be heated to a high temperature.

(I) Use the thermochemical data in Table 4.1 to determine the temperature above which nickel oxide is reduced to nickel according to the following reactions:

Table 4.1 Thermochemical standard data for selected substances, valid for the reference temperature 298.15 K

Substance	$\Delta h_f^\ominus$ (kJ mol^{-1})	$s^\ominus$ (J K^{-1} mol^{-1})
Ni(s)	0	29.9
NiO(s)	−239.7	38.0
C(s)	0	5.74
CO(g)	−110.5	197.7
CO_2(g)	−393.5	216.8
O_2(g)	0	205.2

You may assume that reaction enthalpies and entropies are constant over the whole

$$2NiO(s) + C(s) \rightarrow 2Ni(s) + CO_2(g) \quad |\Delta g_1^\ominus \qquad (4.23)$$

$$NiO(s) + C(s) \rightarrow Ni(s) + CO(g) \quad |\Delta g_2^\ominus \qquad (4.24)$$

temperature range. (2 marks)

(II) Plot the Gibbs free energy of reaction as a function of temperature for each of the following reactions:

$$2\text{Ni(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{NiO(s)} \quad |\Delta g_3^\ominus \tag{4.25}$$

$$\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad |\Delta g_4^\ominus \tag{4.26}$$

$$2\text{C(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO(g)} \quad |\Delta g_5^\ominus \tag{4.27}$$

Interpret this Ellingham diagram and use it to determine the temperature above which nickel oxide is reduced by carbon. (2 marks)

c.

(i) Dimethyl ether (CH_3–O–CH_3) is a possible replacement for diesel fuel. Dimethyl ether is produced from methanol using a suitable catalyst:

$$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$$

Measurements of the equilibrium K constant as a function of temperature yield the following empirical law:

$$\ln K(T) = \frac{2051.7}{\frac{T}{\text{K}}} - 1.5587 \tag{5.99}$$

I. Determine the molar heat of reaction Δh_r and the reaction enthalpy Δs_r of the reaction. You may assume that both Δh_r and Δs_r are constant within the temperature range 498 to 623K. (2 marks)

II. 2 g methanol are filled in a vessel with a volume of 1 dm^3. The vessel, containing a catalyst, is sealed and heated to 250^o C and the chemical equilibrium is established according to Eq. (5.99). Calculate the equilibrium partial pressures of the gases assuming ideal behavior. (2 marks)

(ii) Take $z = xy$ and show that the three partial derivatives conform to the cycle rule. (1 mark)

(iii) Calculate the work done on a closed system consisting of 50.00 g of argon, assumed ideal, when it expands isothermally and reversibly from a volume of 5.000 L to a volume of 10.00 L at a temperature of 298.15 K. Calculate the integral of dP for the same process. (2 marks)

(iv) Consider a reversible process with the same initial and final states as the process with a different path. Calculate the work done on the ideal gas system. if it is reversibly cooled at constant volume of 5.000 L from 298.15 K to 200.00 K, then reversibly expanded from 5.000 L to 10.00 L at a constant temperature of 200.0 K, and then reversibly heated at a constant volume of 10.00 L from 200.0K to 298.15 K. (1 mark)

d. (i) Find a formula for ΔH for the heating of a sample of a gas from temperature T_1 to temperature T_2 at constant pressure if Cpm is represented by Cpm - $a + bT + cT^{-2}$ (1 mark)

(ii) Find ΔH and q for the heating of 2.000 mol of oxygen gas from 25.00◦C to 100.00◦C at a constant pressure of 1.000 atm. (1 mark)

(iii) Calculate ΔH for the change of state of 1.000 mol of helium from a volume of 5.000 L and a temperature of 298.15 K to a volume of 10.000 L and a temperature of 373.15 K. Assume that $C_{P,m} = 5R/2$ and assume that the gas is ideal. (1 mark)

QUESTION TWO (20 marks)

a. (i) Two moles of an ideal gas are allowed to expand reversibly and Isothermally at 300 K from a pressure of 1 atm to a pressure of 0.1 atm. What is the change in Gibbs free energy?. (3 marks)

(ii) Distinguish the following

(I) reversible and irreversible processes (2 marks)

(II) a diabetic and isothermal processes (2 marks)

(iii) One mole of nitrogen at 300k and 20 atmosphere expands to 2 atmospheres. Calculate assuming ideal behavior W, Q, ΔE,and ΔH if the expansion were

(I) isothermal and reversible (2 marks)

(II) Isothermal and irreversible (2 marks)

(III) Adiabatic reversible (2 marks)

(IV) Adiabatic reversible (2 marks)

Also calculate the final volume of the gas in each case. Given Cvm = 20.8116 jk-1mol^{-1} and cpm = 29.13 jk^{-1}mol^{-1}

b.

(i) Write short notes complete differential and homogenous functions (4 marks)

(ii) Calculate the entropy change of the system, the surroundings, and the universe for the Process of Example 2.28. Assume that the surroundings remain at equilibrium at −15.00◦C.

(1 marks)

QUESTION THREE (20 marks)

a. (i) Write short notes on trouton's rule and it's modification (2 marks)

(ii) Use Trouton's rule to estimate $\Delta_{vap}H$ for methane from its normal boiling temperature, −164◦C. Compare with the correct value in Table A.7 of the Appendix (1 mark)

(iii) Without doing any detailed calculations, specify for each process whether each of the following quantities is positive, negative, or equal to zero: q, w, ΔU, ΔS, and ΔS_{surr}.

I. The system consisting of two large objects and a small bar between them is allowed to come to equilibrium from an initial state in which the two objects are at different temperatures. Assume that the objects have fixed volume. (1 mark)

II. A sample of water is boiled at 100°C and 1.00 atm. (1 marks)

(iv)

I. Find an expression for $(\partial S/\partial V)T$,n for n moles of a gas obeying the truncated virial equation of state

$$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m}$$

where B_2 is a function of T and where V_m is the molar volume. (1 mark)

II. Evaluate the expression for $(\partial S/\partial V)_{T,n}$ for 1.000 mol of argon in 25.00 L at 298.15 K. At this temperature, $B2 = -15.8$ cm3 mol^{-1} and $dB_2/dT = 0.25 \times 10^{-6}$ m^3 mol^{-1} K^{-1}. (1 mark)

III. Find an expression for ΔS for an isothermal volume change for n moles of a gas Obeying the truncated virial equation of state in part I. Compare your result with the Corresponding equation for an ideal gas. (1 mark)

IV. Find the value of ΔS for expanding 1.000 mol of argon isothermally at 298.15K from 25.00 L to 50.00 L. Compare the result with the result assuming argon to be an ideal gas. (1 mark)

b. (i) Write short notes on the important properties of a refrigerant (3 marks)

(ii) A refrigeration machine operating at a condenser temperature of 290 K needs 1 kW of power per ton of refrigeration. Determine the following:

I. The coefficient of performance (1 mark)

II.The heat rejected to the condenser (1 mark)

III. The lowest temperature that can be maintained (1 mark)

(ii) Calculate ΔS, ΔS surr, and ΔS univ if 2.000 mol of argon (assume ideal) expands Isothermally and irreversibly at 298.15K from a volume of 10.00 L to a volume of 40.00 L at a constant external pressure of 1.000 atm. Assume that P(transferred) _ P_{ext} and that the surrounding remain at equilibrium at 298.15 K. (2 marks)

c)) i) Derive formulas for the critical temperature and critical molar volume for gas obeying the Van der Waals equation of state. (2 marks)

ii) Show that for a reversible adiabatic process the van der Waals gas obeys (1 mark)

$$C_V dT = -\frac{nRT}{V - nb} dV$$

QUESTION FOUR (20 marks)

(a) (i) A valve on a well-insulated steam pipe carrying saturated steam at 1000 kPa is found Leaking. The temperature of the steam escaping from the leak is measured to be 398 K. Determine the quality of steam flowing through the pipe. The following data are taken from the steam tables: Enthalpy of saturated vapour at 1000 pKa = 2778kJ/kg; Enthalpy of saturated liquid at 1000 pKa = 763 kJ/kg; Enthalpy of superheated steam at 398 K 101.3 pKa = 2726 kJ/kg. (2 marks)

(ii) Write a note on "Carnot's Cycle". (3marks)

(iii) An ideal gas (molecular weight = 29, g =1.4) is contained in a tank of volume 1 m^3 at 10 MPa and 400 K. The gas is discharged into the surrounding atmosphere by opening a valve. The valve is closed when the pressure inside the tank falls to 5 MPa. If the surrounding atmosphere is at 101.3 pKa, determine the temperature of the gas in the tank and the mass of gas discharged. (3 marks).

(b) (i) Show that $(^{\Delta E}/_{\Delta V})_T = 0$. (3marks)

(ii) Calculate the difference in molar entropy and molar free energy

(I) between liquid water at -5°c and ice at -5 °c (3 marks)

(II) Between liquid water and water vapour at 95°C and 1 atm. distinguish between ΔS_{System} and ΔS surrounding. (3 marks)

(iii) One mole of an ideal gas originally at volume of 5 liters at 500k is allowed to expand adiabatically until the final volume is 15litres. For gas $C_v = \frac{3}{2}R$. Calculate final temperature

and ΔS when

(I) the expansion take place reversibly. (1 mark)

(II) The expansion takes place against a constant pressure of 3atm. (1 mark)

(III) The change in volume is due to a free expansion. (1 mark)

Table A.7 Specific Enthalpy Changes of Fusion and Vaporization

Substance	M.P./°C	$\Delta_{fus}H_m/J\,g^{-1}$	B.P./°C	$\Delta_{vap}H_m/J\,g^{-1}$
Ammonia	66.7		−33.35	1372
Benzene	5.5	127	80.1	394
Carbon dioxide	−56.6[a]	180.7	−78.5[b]	526.6
Carbon monoxide	−199	29.8	−191.5	240.98
Carbon tetrachloride	−22.99	17.5	76.54	207.5
Ethane	−183.3	95.10	−88.6	520.32
Ethanol	−117.3	109.0	78.5	878.58
Methane	−182	58.41	−164	555.19
Water	0.0	333.5	100.0	2257.5

From R. C. Weast, *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, pp. B227ff, C691ff.

[a]At 5.2 atm pressure.
[b]Sublimation temperature at 1.000 atm pressure.

Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	1 kg m^{-1} s^{-2} 1 N m^{-2}	pascal, Pa
Energy	1 kg m^2 s^{-2} 1 N m 1 Pa m^3	joule, J
Power	1 kg m^2 s^{-3} 1 J s^{-1}	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

Table F.3 Common SI prefixes

Prefix	y	z	a	f	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}
Prefix	**da**	**h**	**k**	**M**	**G**	**T**	**P**	**E**	**Z**	**Y**
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^{2}	10^{3}	10^{6}	10^{9}	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

PERIODIC TABLE OF THE ELEMENTS

Metals
Nonmetals
Metalloids

	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIIIB 8	VIIIB 9	VIIIB 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	0 18
1	1 H 1.008																1 H 1.008	2 He 4.0026
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.9984	10 Ne 20.1797
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.085	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9058	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.9045	54 Xe 131.293
6	55 Cs 132.9055	56 Ba 137.327	57 La 138.9055 *	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.084	79 Au 196.9666	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227) **	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

*Lanthanide Series

58 Ce 140.116	59 Pr 140.9076	60 Nd 144.242	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.500	67 Ho 164.9303	68 Er 167.259	69 Tm 168.9342	70 Yb 173.054	71 Lu 174.9668

** Actinide Series

90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.

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