

UNIVERSITY OF SWAZILAND  
BACHELOR OF SCIENCE

SUPPLEMENTARY EXAMINATION 2005

TITLE OF PAPER : PHYSICAL CHEMISTRY

COURSE NUMBER : C202

TIME : 3 HOURS

INSTRUCTIONS : THERE ARE SIX QUESTIONS

: ANSWER ANY FOUR QUESTIONS

: BEGIN THE ANSWER TO EACH QUESTION  
ON A SEPARATE SHEET OF PAPER

: DATA SHEETS ARE PROVIDED WITH THIS  
EXAMINATION PAPER

DO NOT OPEN THIS PAPER UNTIL THE INVIGILATOR INSTRUCTS YOU TO  
DO SO.

**QUESTION 1 [25 MARKS]**

- a) Write short notes on any Two of the following models of gas behaviour: [10]
- Van der Waals equation
  - Dieterici equation
  - Berthelots equation
  - Virial equation
- b) A model of a non-ideal gas states:

$$P = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$$

Obtain expressions for the critical constants  $V_{m,c}$ ,  $T_c$  and  $P_c$ . [15]

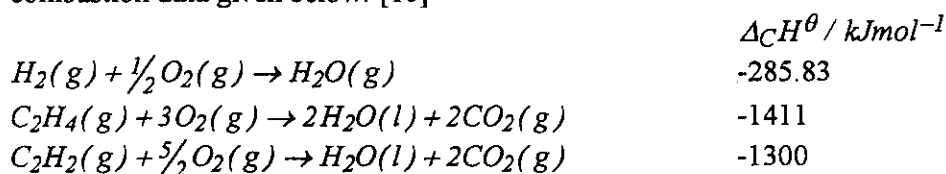
**QUESTION 2 [25 MARKS]**

Adiabatic expansion of an ideal gas is quite different from isothermal expansion.

- a) Explain what is meant by adiabatic expansion, draw an adiabat and an isotherm on a P versus V graph and compare them. [5]
- b) Derive the expression for the change in temperature of an adiabatic expansion of an ideal gas against constant external pressure from  $V_i$  to  $V_f$ . [5]
- c) A sample of argon at 1.0 atm pressure and 25°C expands reversibly and adiabatically from 0.50 L to 1.00 L. Calculate: [15]
- its final temperature
  - the work done during the expansion and
  - the change in internal energy.

**QUESTION 3 [25 MARKS]**

- a) Write a general expression for Hess's Law. [6]
- b) Using Hess's Law calculate the standard enthalpies of the following reactions:
- $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  [3]
  - $\text{C}_6\text{H}_{12}$  {Cyclohexane} (l) +  $\text{H}_2$  (g)  $\rightarrow$   $\text{C}_6\text{H}_{14}$  {n-hexane} (l) [3]
  - $2\text{HN}_3$  (l) +  $2\text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 4\text{N}_2$  (g). [3]
- c) Calculate the enthalpy of hydrogenation and the internal energy change of hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion data given below: [10]



**Question 4 [25 Marks]**

a) Write short notes on **Any Two** of the following concepts:

- i) Statistical view of entropy [5]
- ii) Clausius inequality [5]
- iii) Second law of thermodynamics [5]
- iv) Third law of thermodynamics [5]

For each concept include the origin or a short derivation showing its origin, an example where applicable and the role or implication of each of the concepts in thermodynamics.

- b) (i) Using an illustration of your choice define fugacity [5]  
 (ii) Using the following chemical potential expression for ideal and real gases

$$\mu_2 = \mu_1^\theta + RT \ln \left( \frac{p_2}{p_1^\theta} \right) \text{ and } \mu_2 = \mu_1^\theta + RT \ln \left( \frac{f_2}{f_1^\theta} \right), \text{ respectively.}$$

Derive the fugacity expression

[5]

$$f = p \exp \int_{p_1}^{p_2} \left\{ \frac{Z(p, T) - 1}{p} \right\} dp$$

- (iii) Given that fugacity is given by the expression: [5]

$$f = p \exp \int_{p_1}^{p_2} \left\{ \frac{Z(p, T) - 1}{p} \right\} dp$$

Evaluate fugacity of  $O_2$  at 200 K given that the compression factor of  $O_2$  is 0.98796 at 4.00000 atm.

**QUESTION 5 [25 MARKS]**

- a) Draw a sketch of the phase diagram of carbon dioxide and explain briefly the slopes and curvature of the liquid-solid and the liquid-gas boundaries, respectively. [10]

- b) i) Derive the Clausius-Clapeyron equation for evaporation in the form

$$\frac{d(\ln p)}{dT} \quad [10]$$

- ii) The triple point of benzene is at  $5.5^\circ\text{C}$  and 36 mm Hg. Predict the boiling point of benzene at 0.1 atm pressure. [5]

**QUESTION 6 [25 MARKS]**

a) Write short notes on Any Two of the following: [10]

- i) Phase rule
- ii) Eutectic temperature
- iii) Freezing point depression
- iv) Boiling point elevation
- v) Azeotrope

b) i) Using the chemical potential expression:

$$\mu_A = \mu_A^* + RT \ln \chi_A$$

where  $\mu_A^*$  is the chemical potential of the pure solvent A, derive the expression for the boiling point elevation in terms of the boiling point of the pure solvent  $T$ , its enthalpy of evaporation and the molality of the solute  $m_s$ . [5]

- c) i) What is the approximate relative molecular mass of compound X if 1.00g of X added to 20.0 g benzene leads to a freezing point depression of  $1.51^\circ\text{C}$ ? [5]
- ii) Why is the freezing point depression preferred to boiling point elevation for the determination of relative molecular masses? [2]
- iii) Why would benzene be a better solvent to use than methanol? [3]



# THE PERIODIC TABLE OF ELEMENTS

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VI	VII	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
Period 1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.9	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.9	26 Fe 55.85	27 Co 58.71	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.7	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 91.22	42 Mo 95.94	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 210	85 At 210	86 Rn 222
7	87 Fr 223	88 Ra 226.0	103 Lr 257	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

METALS

METALLOIDS

NON-METALS

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No
	227.0	232.0	231.0	238.0	237.1	239.1	241.1	247.1	249.1	251.1	254.1	257.1	258.1	255

Numbers below the symbol indicates the atomic masses; and the numbers above the symbol indicates the atomic numbers.

Temperature dependence of heat capacities,  $C_{p,m} = a + bT + cT^{-2}$

	M <sub>r</sub>	ΔH <sub>f</sub> <sup>0</sup> /kJ/mol	M <sub>r</sub>	ΔH <sub>f</sub> <sup>0</sup> /kJ/mol	a/J K <sup>-1</sup> mol <sup>-1</sup>	b/10 <sup>-3</sup> J K <sup>-2</sup> mol <sup>-1</sup>	c/10 <sup>5</sup> J kmol <sup>-1</sup>
H <sub>2</sub> O(l)	18.015	-241.8	O <sub>2</sub> (g)	+142.7	Gases (298-2000K)		
H <sub>2</sub> O(g)	18.015	-286.8	NO(g)	+90.2	He, Ne, Ar, Kr, Xe		
H <sub>2</sub> O <sub>2</sub> (l)	34.015	-187.8	NO <sub>2</sub> (g)	+33.2	H <sub>2</sub>	27.28	0
NH <sub>3</sub> (g)	17.031	-46.1	N <sub>2</sub> O <sub>4</sub> (g)	+9.2	O <sub>2</sub>	29.96	3.26
N <sub>2</sub> H <sub>4</sub> (l)	32.045	+50.6	SO <sub>2</sub> (g)	-296.8	N <sub>2</sub>	28.98	-1.67
N <sub>2</sub> H <sub>4</sub> (g)	43.028	+264.1	H <sub>2</sub> S(g)	-20.6	Cl <sub>2</sub>	37.03	4.18
NH <sub>3</sub> (g)	43.028	+294.1	SF <sub>6</sub> (g)	-1209	CO <sub>2</sub>	44.23	3.77
NH <sub>3</sub> (l)	63.013	-174.1	HF(g)	-271.1	CO	42.23	0.67
NH <sub>4</sub> OH(s)	33.030	-114.2	HCl(g)	-92.3	H <sub>2</sub> O	30.54	-2.85
NH <sub>4</sub> Cl(s)	53.492	-314.4	HCl(aq)	-167.2	NH <sub>3</sub>	29.75	8.79
HgCl <sub>2</sub> (s)	271.50	-224.3	HBr(g)	+36.4	H <sub>2</sub> O	23.64	10.29
H <sub>2</sub> SO <sub>4</sub> (l)	98.078	-814.0	H <sub>2</sub> (g)	+26.5	CH <sub>4</sub>	16.86	25.10
H <sub>2</sub> SO <sub>4</sub> (aq)	98.078	-909.3	CO <sub>2</sub> (g)	-393.5	C(s)	23.64	47.86
NaCl(s)	58.443	-411.0	CO(g)	-110.5		16.86	4.77
NaOH(s)	39.997	-426.7	Al <sub>2</sub> O <sub>3</sub> (s)	-1675.7	Standard molar enthalpies of formation and combustion at 298.15 K.		
KCl(s)	74.555	-435.9	SiO <sub>2</sub> (s)	-910.9	CH <sub>4</sub> (g)	16.043	-74.81
KBr(s)	119.011	-392.2	FeS(s)	-100.0	C <sub>2</sub> H <sub>2</sub> (g)	26.038	+226.8
KI(s)	166.006	-327.6	FeS <sub>2</sub> (s)	-178.2	C <sub>2</sub> H <sub>4</sub> (g)	28.054	+52.30
DIATOMICS	Eg. N <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub>	0	AgCl(s)	-127.1	C <sub>2</sub> H <sub>6</sub> (g)	30.070	-141.1
							-1560
Enthalpies of fusion and evaporation ΔH <sub>m</sub> <sup>0</sup> /kJ/mol at the transition temperature							
	T/K	Fusion <sup>a</sup>	T/K	Evaporation <sup>b</sup>			
He	3.5	0.021	4.22	0.084	C <sub>3</sub> H <sub>6</sub> (propene)(g)	42.081	-2091
Ar	83.81	1.188	87.29	6.506	C <sub>3</sub> H <sub>6</sub> (cyclopropane)(g)	42.081	-2058
H <sub>2</sub>	13.96	0.117	20.38	0.9163	C <sub>3</sub> H <sub>8</sub> (n-butane)(g)	58.124	-126.11
O <sub>2</sub>	63.15	0.719	77.35	5.586	C <sub>3</sub> H <sub>12</sub> (n-pentane)(g)	72.151	-146.4
N <sub>2</sub>	54.36	0.444	90.18	6.820	C <sub>6</sub> H <sub>12</sub> cyclohexane (l)	84.163	-156.2
Cl <sub>2</sub>	172.12	6.406	239.05	20.410	C <sub>6</sub> H <sub>14</sub> n-hexane (l)	86.178	-198.7
Br <sub>2</sub>	285.90	10.573	332.35	29.45	C <sub>6</sub> H <sub>6</sub> benzene (l)	78.115	+48.99
I <sub>2</sub>	386.75	15.52	458.39	41.80	C <sub>6</sub> H <sub>16</sub> n-octane (l)	114.233	-3268
Hg	234.29	2.292	629.73	59.296	C <sub>10</sub> H <sub>8</sub> naphthalene (l)	128.175	-249.8
Ag	1234	11.30	2436	250.63	CH <sub>3</sub> CHO (g)	44.054	-5471
Na	370.95	2.601	1156	98.01	CH <sub>3</sub> CH <sub>2</sub> OH (l)	46.070	-5157
CO <sub>2</sub>	217.0	8.33	194.64	25.23	CH <sub>3</sub> COOH (l)	80.053	-726.1
H <sub>2</sub> O	273.15	6.008	373.15	40.656	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> (l)	88.107	-1193
NH <sub>3</sub>	195.40	5.652	239.73	23.351	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> (s)	94.114	-1368
H <sub>2</sub> S	187.61	2.377	212.80	18.673	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (l)	93.129	-726.1
CH <sub>4</sub>	90.68	0.941	111.66	8.18	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> (s)	88.107	-1193
C <sub>2</sub> H <sub>6</sub>	88.85	2.86	184.55	14.7	CH <sub>2</sub> (NH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H, glycine (s)	75.068	-1368
C <sub>6</sub> H <sub>6</sub>	278.65	10.59	353.25	30.8	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> , α-D-glucose (s)	180.159	-726.1
CH <sub>3</sub> OH	175.25	3.159	337.22	35.27	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> , β-D-glucose (s)	180.159	-1368
					C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> , sucrose (s)	342.303	-2808
					CH <sub>3</sub> CH(OH)COOH	90.079	-5645
					lactic acid (s)		-1344
							-694.0

Source: American Institute of Physics handbook, McGraw-Hill.

**Standard molar Gibbs free energy and molar entropy of formation at 298.15 K**

	$M_r$	$\Delta G_f^\theta / \text{KJ/mol}$	$S^\theta / \text{K}^{-1} \text{mol}^{-1}$		$M_r$	$\Delta G_f^\theta / \text{KJ/mol}$	$S^\theta / \text{K}^{-1} \text{mol}^{-1}$
$\text{H}_2\text{O}(\text{g})$	18.015	-228.57	188.83	$\text{O}_3(\text{g})$	47.998	163.2	238.93
$\text{H}_2\text{O}(\text{l})$	18.015	-120.35	109.6	$\text{NO}(\text{g})$	30.006	86.35	210.76
$\text{H}_2\text{O}_2(\text{l})$	34.015	-120.35	109.6	$\text{NO}_2(\text{g})$	46.006	51.31	240.06
$\text{NH}_3(\text{g})$	17.031	-16.45	192.45	$\text{N}_2\text{O}_4(\text{g})$	92.012	97.89	304.29
$\text{N}_2\text{H}_4(\text{l})$	32.045	149.43	121.21	$\text{SO}_2(\text{g})$	64.063	-300.19	248.22
$\text{N}_2\text{H}_4(\text{g})$	32.045	149.43	121.21	$\text{H}_2\text{S}(\text{g})$	34.080	-33.56	205.79
$\text{N}_3\text{H}(\text{l})$	43.028	327.3	140.6	$\text{SF}_6(\text{g})$	146.054	-1105.3	291.82
$\text{N}_3\text{H}(\text{g})$	43.028	328.1	155.60	$\text{HF}(\text{g})$	20.006	-273.2	173.78
$\text{HNO}_3(\text{l})$	63.013	-80.71	155.60	$\text{HCl}(\text{g})$	36.461	-95.30	186.91
$\text{NH}_2\text{OH}(\text{g})$	33.030	-202.87	94.6	$\text{HBr}(\text{g})$	80.917	-53.45	198.70
$\text{H}_2\text{SO}_4(\text{l})$	98.078	-690.00	156.90	$\text{HI}(\text{g})$	127.912	1.70	206.59
$\text{H}_2\text{SO}_4(\text{aq})$	98.078	-744.53	20.1	$\text{CO}_2(\text{g})$	44.010	-394.36	213.74
$\text{NaCl}(\text{s})$	58.443	-384.14	72.13	$\text{CO}(\text{g})$	28.011	-137.17	197.67
$\text{NaOH}(\text{s})$	39.997	-379.49	64.46	$\text{Al}_2\text{O}_3(\text{s})$	101.945	-1582.3	50.92
$\text{KCl}(\text{s})$	74.555	-409.14	82.59	$\text{SiO}_2$	60.09	-856.64	41.84
$\text{KBr}(\text{s})$	119.011	-380.66	95.90	$\text{FeS}(\text{s})$	87.91	-100.4	60.29
$\text{KI}(\text{s})$	166.006	-324.89	106.32	$\text{FeS}_2(\text{s})$	119.975	-166.9	52.93
				$\text{AgCl}(\text{s})$	143.323	-109.79	96.2
$\text{H}_2(\text{g})$	4.003	0	126.15	$\text{H}_2(\text{g})$	200.59	31.82	174.96
$\text{Ar}(\text{g})$	39.95	0	154.84	$\text{He}(\text{g})$	200.59	0	76.02
$\text{H}_2(\text{g})$	2.016	0	130.684	$\text{Ar}(\text{g})$	107.87	245.65	173.00
$\text{N}_2(\text{g})$	28.013	0	191.61	$\text{Ag}(\text{g})$	107.87	0	42.55
$\text{O}_2(\text{g})$	31.999	0	205.138	$\text{Na}(\text{g})$	370.95	76.76	153.71
$\text{O}_3(\text{g})$	47.998	163.2	238.93	$\text{Na}(\text{g})$	22.99	0	51.21
$\text{Cl}_2(\text{g})$	70.91	0	223.07				
$\text{Br}_2(\text{l})$	159.82	3.110	245.46				
$\text{Br}_2(\text{g})$	159.82	0	152.23				
$\text{I}_2(\text{g})$	253.81	19.33	260.69				
$\text{I}_2(\text{s})$	253.81	0	116.135				
				organic compounds	$M_r$	$\Delta G_f^\theta / \text{KJ/mol}$	$S^\theta / \text{K}^{-1} \text{mol}^{-1}$
				$\text{CH}_4(\text{g})$ methane	16.043	-50.72	186.26
				$\text{C}_2\text{H}_2(\text{g})$ ethyne	26.038	209.20	200.94
				$\text{C}_2\text{H}_4(\text{g})$ ethene	28.05	68.15	219.56
				$\text{C}_2\text{H}_6(\text{g})$ ethane	30.070	-32.82	229.60
				$\text{C}_3\text{H}_6$ cyclopropane(g)	42.081	104.45	237.55
				$\text{C}_3\text{H}_6$ propene(g)	42.081	62.78	267.05
				$\text{C}_4\text{H}_{10}$ n-butane (g)	58.124	-17.03	310.23
				$\text{C}_5\text{H}_{12}$ n-pentane(g)	72.151	-8.20	348.40
				$\text{C}_6\text{H}_{14}$ n-hexane (l)	84.163	26.8	
				$\text{C}_6\text{H}_{12}$ cyclohexane (l)	84.163	26.8	
				$\text{C}_6\text{H}_6$ benzene (l)	78.115	124.3	173.3
				$\text{C}_8\text{H}_{18}$ n-octane (l)	114.233	129.72	269.31
				$\text{C}_{10}\text{H}_8$ naphthalene (l)	128.175	6.4	361.1
				$\text{CH}_3\text{OH}(\text{g})$	32.042	-161.96	239.81
				$\text{CH}_3\text{OH}(\text{l})$	32.042	-166.27	126.8
				$\text{CH}_3\text{CHO}(\text{g})$	44.054	-128.86	250.3
				$\text{CH}_3\text{COOH}(\text{l})$	60.053	-389.9	159.8
				$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$	88.107	-332.7	259.4
				$\text{C}_6\text{H}_5\text{OH}(\text{g})$	94.114	-50.9	146.0
				$\text{C}_6\text{H}_5\text{NH}_2(\text{l})$	93.129		
				$\text{CH}_3\text{NH}_2\text{CO}_2\text{H}$ glycine (s)	75.068	-373.4	103.5
				$\text{C}_6\text{H}_{12}\text{O}_6$ D-D-glucose (s)	180.159		
				$\text{C}_6\text{H}_{12}\text{O}_6$ D-D-glucose (s)	180.159	-910	212
				$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ sucrose (s)	342.303	-1543	360.2
				$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	90.079		
				lactic acid (s)			

Source: American Institute of Physics handbook, McGraw-Hill.

## Heat capacities at 25°C

	$C_{v,m}$	$C_{p,m}$
	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$
He, Ne, Ar, Kr, Xe	12.47	20.78
H <sub>2</sub>	20.50	28.81
O <sub>2</sub>	21.01	29.33
N <sub>2</sub>	20.83	29.14
CO <sub>2</sub>	28.83	37.14
NH <sub>3</sub>	27.17	35.48
CH <sub>4</sub>	27.43	35.74
NO <sub>2</sub>		77.28
NO		37.20

## F.P. Depression, B.P. Elevation

Solvent	F.P. °C	$K_f$ °C kg mol <sup>-1</sup>	B.P. (°C, 101 kNm <sup>-2</sup> )	$K_b$ °C kg mol <sup>-1</sup>
Water	0	1.86	100.0	0.52
Benzene	5.51	5.10	80.1	2.60
Acetic Acid	16.6	3.90	118.1	3.10
Cyclohexane	6.5	20.2	81.4	2.79
Camphor	177.7	40.0	205	-
Nitrobenzene	5.7	6.9	210.9	5.24
Ethanol	-177		78.5	1.22
Chloroform	-64		61.3	3.63

Third Law entropies at 25°C,  $\text{Sm}^0/\text{J K}^{-1} \text{mol}^{-1}$ 

Solids		Liquids		Gases	
Ag	42.68	Hg	76.02	H <sub>2</sub>	130.6
C(gr)	5.77	Br <sub>2</sub>	152.3	N <sub>2</sub>	192.1
C(d)	2.44			O <sub>2</sub>	205.1
Cu	33.4			Cl <sub>2</sub>	223.0
Zn	41.6	H <sub>2</sub> O	70.0		
I <sub>2</sub>	116.7			CO <sub>2</sub>	213.7
S(Rh)	31.9	HNO <sub>3</sub>	155.6	HCl	186.8
				H <sub>2</sub> S	205.6
AgCl	96.2	C <sub>2</sub> H <sub>5</sub> OH	161.0	NH <sub>3</sub>	192.5
AgBr	104.6	CH <sub>3</sub> OH	126.7	CH <sub>4</sub>	186.1
CuSO <sub>4</sub> ·5H <sub>2</sub> O	305.4	C <sub>6</sub> H <sub>6</sub>	49.03	C <sub>2</sub> H <sub>6</sub>	229.4
HgCl <sub>2</sub>	144	CH <sub>3</sub> COOH	159.8	CH <sub>3</sub> CHO	265.7
Sucrose	360.2	C <sub>6</sub> H <sub>12</sub>	298.2		