UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2014/2015 Academic Session

June 2015

# EKC 108 – Physical and Analytical Chemistry
## *[Kimia Fizik dan Kimia Analisis]*

Duration : 3 hours
*[Masa : 3 jam]*

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

*[Sila pastikan bahawa kertas peperiksaan ini mengandungi TUJUH muka surat yang bercetak dan EMPAT muka surat Lampiran sebelum anda memulakan peperiksaan ini.]*

**Instruction:** Answer **ALL** questions.

*[**Arahan:** Jawab **SEMUA** soalan.]*

In the event of any discrepancies, the English version shall be used.

*[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai].*

...2/-

Answer ALL questions.

1. [a] Describe how stray radiation can lead to deviation from Beer's law. Sketch a graph to illustrate stray radiation.

*[8 marks]*

[b] Outline a general method if a standard addition method was to be used in determining an analyte of concern. Sketch the diagram.

*[5 marks]*

[c] Copper and zinc were determined by forming coloured complexes with 2-pyridyl-azo-resorcinol (PAR). The absorbances for PAR, a mixture of $Cu^{2+}$ and $Zn^{2+}$ and standards of 1.0 ppm $Cu^{2+}$ and 1.0 ppm $Zn^{2+}$ are listed in Table Q.1.

Determine the molar concentration of each analyte in the mixture.

Table Q.1.

| Wavelength (nm) | Absorbance | | | |
|---|---|---|---|---|
| | PAR | $Cu^{2+}$ std | $Zu^{2+}$ std | Mixture |
| 480 | 0.211 | 0.698 | 0.971 | 0.656 |
| 496 | 0.137 | 0.732 | 1.018 | 0.668 |
| 510 | 0.100 | 0.732 | 0.891 | 0.627 |
| 526 | 0.072 | 0.602 | 0.672 | 0.498 |
| 540 | 0.056 | 0.387 | 0.306 | 0.290 |

*[12 marks]*

2. [a] Substances *A* and *B* have retention times of 16.40 and 17.63 min, respectively, in a 30 cm column. An unretained species passes through the column in 1.30 min. The peak widths (at base) for *A* and *B* are 1.11 and 1.21 min, respectively. Calculate:

[i] the column resolution.

*[3 marks]*

[ii] the average number of plates in the column.

*[3 marks]*

[iii] the plate height.

*[3 marks]*

[iv] the length of column required to achieve a resolution of 1.5.

*[3 marks]*

[v] the time required to elute substance *B* in the column if the $R_s$ value is 1.5.

*[3 marks]*

...3/-

*Jawab <u>SEMUA</u> soalan.*

1. [a] *Terangkan bagaimana sinaran kesesar boleh menyisih daripada Hukum Beer. Lakarkan geraf untuk menggambarkan sinaran sesat.*

[8 markah]

[b] *Gariskan tatacara umum sekiranya kaedah pertambahan piawai digunakan dalam penentuan sesuatu analit. Lakarkan gambarajah.*

[5 markah]

[c] *Tembaga dan zink ditentukan dengan membentuk komplek-komplek berwarna dengan 2-piridil-azo-resorsinol (PAR). Daya serap bagi PAR, suatu campuran $Cu^{2+}$ dan $Zn^{2+}$ dan piawai 1.0 ppm $Cu^{2+}$ dan 1.0 ppm $Zn^{2+}$ adalah seperti dalam Jadual S.1.*

*Tentukan kepekatan molar setiap analit dalam campuran tersebut.*

*Jadual S.1.*

| *Jarak gelombang* (nm) | *Daya serap* | | | |
|---|---|---|---|---|
| | PAR | $Cu^{2+}$ std | $Zu^{2+}$ std | *Campuran* |
| 480 | 0.211 | 0.698 | 0.971 | 0.656 |
| 496 | 0.137 | 0.732 | 1.018 | 0.668 |
| 510 | 0.100 | 0.732 | 0.891 | 0.627 |
| 526 | 0.072 | 0.602 | 0.672 | 0.498 |
| 540 | 0.056 | 0.387 | 0.306 | 0.290 |

[12 markah]

2. [a] *2 bahan* A *dan* B *mempunyai waktu penahanan 16.40 dan 17.63 min masing-masing di dalam turus 30 sm. Spesis yang tak tersimpan bergerak melalui turus dalam masa 1.3 min. Lebar puncak (di bawah) bagi* A *dan* B *ialah 1.11 dan 1.21 min masing-masing. Kirakan:*

[i] *peleraian turus.*

[3 markah]

[ii] *purata nombor plat di dalam turus.*

[3 markah]

[iii] *ketinggian plat.*

[3 markah]

[iv] *panjang turus yang diperlukan untuk mencapai peleraian 1.5.*

[3 markah]

[v] *masa yang diperlukan untuk mengelut bahan* B *di dalam turus sekiranya nilai* $R_s$ *adalah 1.5.*

[3 markah]

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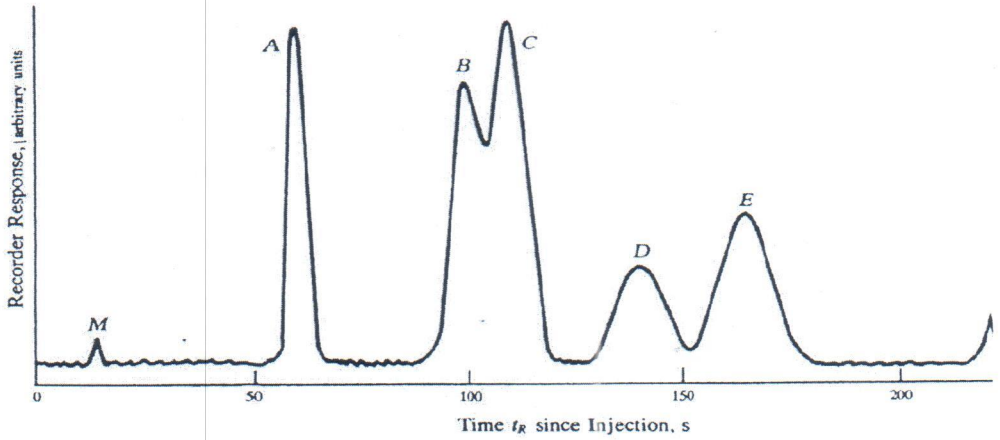
[b]




[i] Why did peak *B* and *C* combine? Explain.

*[5 marks]*

[ii] How to improve the column resolution?

*[5 marks]*

3. Ethane gas is placed inside a piston at 350 K and 70 bar. Calculate,

[a] Molar volume by assuming ethane as an ideal gas.

*[2 marks]*

[b] Molar volume if ethane is a real gas.

*[4 marks]*

[c] Compressibility factor of the gas using your answer in Q.3.[a] and Q.3.[b].

*[2 marks]*

[d] Pressure and molar volume when the compressibility factor becomes greater than unity. Show an appropriate diagram.

*[6 marks]*

[e] Work, $w$, required (in kJ/mol) for the real ethane to attain an ideal gas condition. Show an appropriate diagram.

*[6 marks]*

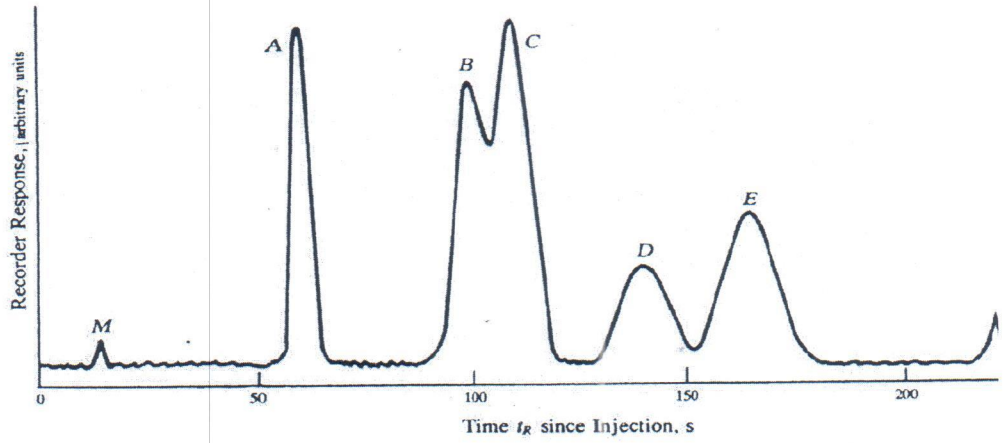
[f] Heat, $q$ (in kJ/mol), for the real ethane gas to attain an ideal behavior.

*[2 marks]*

[g] Entropy change, $\Delta S$, for the real ethane gas to attain an ideal behavior. State the reversibility of the process.

*[3 marks]*

[b]




*[i]* *Mengapa puncak* B *dan* C *bersatu? Terangkan.*

[5 markah]

*[ii]* *Bagaimanakah untuk mempertingkatkan peleraian bagi turus?*

[5 markah]

3. *Gas etana diletakkan di dalam omboh pada 350 K dan 70 bar. Kirakan,*

*[a]* *Isipadu molar dengan andaian, etana ialah gas unggul.*

[2 markah]

*[b]* *Isipadu molar sekiranya etana ialah gas sebenar.*

[4 markah]

*[c]* *Faktor kemampatan gas tersebut menggunakan jawapan anda di S.3.[a] dan S.3.[b].*

[2 markah]

*[d]* *Tekanan dan isipadu molar apabila faktor kemampatan menjadi lebih besar dari satu. Tunjukkan gambarajah bersesuaian.*

[6 markah]

*[e]* *Kerja,* w, *yang diperlukan (dalam kJ/mol) bagi etana sebenar untuk mencapai keadaan gas unggul. Tunjukkan gambarajah bersesuaian.*

[6 markah]

*[f]* *Haba,* q *(dalam kJ/mol), bagi gas etana sebenar untuk mencapai sifat keunggulan.*

[2 markah]

*[g]* *Perubahan entropi, $\Delta S$, bagi gas etana sebenar untuk mencapai sifat keunggulan. Nyatakan kebolehbalikan proses ini.*

[3 markah]

4. For zinc-oxygen fuel cell,

[a] Write the reaction at anode.

*[4 marks]*

[b] Write the reaction at cathode.

*[4 marks]*

[c] Write the overall reaction.

*[4 marks]*

[d] Calculate emf (volts) of the half reaction occurred at cathode. Given, $\Delta G°(O_2) = 0$ kJ/mol, $\Delta G°(OH^-) = -157.244$ kJ/mol
$\Delta G°(H_2O) = -237.129$ kJ/mol

*[6 marks]*

[e] Calculate emf (volts) at anode if the cell potential is 1.646 V.

*[3 marks]*

[f] How much additional voltage can be obtained if the cell is replaced with magnesium as its fuel?

*[4 marks]*

4. *Bagi sel bahanapi zink-oksigen,*

*[a]* *Tuliskan tindakbalas pada anod.*

[4 markah]

*[b]* *Tuliskan tindakbalas pada katod.*

[4 markah]

*[c]* *Tuliskan tindakbalas keseluruhan.*

[4 markah]

*[d]* *Kirakan emf (volt) tindakbalas separa yang berlaku di katod. Diberikan,*
$\Delta G°(O_2) = 0$ *kJ/mol,* $\Delta G°(OH) = -157.244$ *kJ/mol*
$\Delta G°(H_2O) = -237.129$ *kJ/mol*

[6 markah]

*[e]* *Kirakan emf (volt) pada anod sekiranya potensi sel ialah 1.646 V.*

[3 markah]

*[f]* *Berapakah voltan tambahan yang boleh diperolehi sekiranya sel diganti dengan magnesium sebagai bahanapi?*

[4 markah]

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Appendix

Sistem penukaran unit

| Kuantiti | Nilai kesamaan |
|---|---|
| Jisim | 1 kg = 1000 g = 0.001 tan metrik = 2.20462 $Ib_m$ = 35.27392 aun<br>1 $Ib_m$ = 16 aun = $5\times10^{-4}$ tan = 453.593 g = 0.453593 kg |
| Panjang | 1 m = 100 sm = 1000 mm = $10^6$ μm = $10^{10}$ angstrom = 39.37 in<br>= 3.2808 ka = 1.0936 ela = 0.0006214 batu. |
| Isipadu | 1 $m^3$ = 1000 L = $10^6$ $sm^3$ = $10^6$ml<br>= 35.3145 $ka^3$ = 264.17 gal<br>1 $ka^3$ = 1728 $in^3$ = 7.4805 gal = 0.028317 $m^3$ = 28.317 L = 28317 $sm^3$ |
| Daya | 1 N = 1 kg.m.$s^{-2}$ = $10^5$ dyne = $10^5$ g.sm.$s^{-2}$ = 0.22481 $Ib_f$<br>1 $Ib_f$ = 32.174 $Ib_m$ ft.$s^{-2}$ = 4.4482 N |
| Tekanan | 1 atm = $1.01325\times10^5$ $N/m^2$ (Pa) = $1.01325\times10^5$ kg/(m.$s^2$) = 760 torr<br>= 760 mmHg = 14.696 psi = 1.01325 bar |
| Tenaga | 1 J = 1 N.m = $10^7$ dyne.sm = $2.778\times10^{-7}$ kW.h = 0.23901 kal<br>= 0.7376 ka-$Ib_f$ = $9.486\times10^{-4}$ Btu |
| Kuasa | 1 W = 1 J/s = 0.23901 kal/s = 0.7376 ka-$Ib_f$/s = $9.486\times10^{-4}$ Btu/s<br>= $1.341\times10^{-3}$ hp |

Pemalar dan persamaan

| Pemalar Gas | Pemalar Faraday | Persamaan-persamaan |
|---|---|---|
| 8.314 $m^3$.Pa/mol.K<br>0.08314 liter. bar/mol.K<br>0.08206 liter.atm/mol.K<br>62.36 liter.mmHg/mol.K<br>0.7302 $ft^3$.atm/Ib-mole.°R<br>10.73 $ft^3$.psia/Ib-mole.°R<br>82.06 $cm^3$.atm/mol.K<br>8.314 J/mol.K<br>1.987 kal/mol.K<br>1.987 Btu/Ib-mole.°R | 96485 C/mol | $\Delta A = \Delta U - T\Delta S$<br>$\Delta G = \Delta H - T\Delta S$<br>$K_P^o = \prod_i \left(P_{i,eq}/P^o\right)^{v_i}$<br>$\zeta^o = -\frac{\Delta G^o}{nF}$<br>$\zeta = \zeta^o - \frac{RT}{nF}\ln\left[\prod_i (a_i)^{v_i}\right]$<br>$= \zeta^o - \frac{RT}{nF}\ln Q$<br>$\left(P + \frac{a}{V_m^{\,2}}\right)(V_m - b) = RT$<br>$a = \frac{27R^2T_c^{\,2}}{64P_c}$ , $b = \frac{RT_c}{8P_c}$<br>$\left(\frac{[A]}{[A]_o}\right)^{1-n} = 1 + [A]_o^{n-1}(n-1)k_a t$ untuk n ≠ 1. |

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Pemalar kritikal

| Gas | $T_c$ (K) | $P_c$ (bar) | Gas | $T_c$ (K) | $P_c$ (bar) |
|---|---|---|---|---|---|
| $H_2$ | 33.2 | 13.0 | $CH_4$ | 190.6 | 46.0 |
| He-4 | 5.2 | 2.27 | $C_2H_6$ | 305.4 | 48.9 |
| $N_2$ | 126.2 | 34.0 | $C_3H_8$ | 369.8 | 42.5 |
| $O_2$ | 154.6 | 50.5 | $C_4H_{10}$ (*n*) | 425.2 | 38.0 |
| $Cl_2$ | 417 | 77.0 | $C_4H_{10}$ (*iso*) | 408.1 | 36.5 |
| Bromin | 584 | 103.0 | Ethylena | 282.4 | 50.4 |
| Ammonia | 405.6 | 113.0 | Propylena | 365.0 | 46.3 |
| $H_2O$ | 647.1 | 220.5 | $CO_2$ | 304.2 | 73.8 |

Standard electrode potential

| Half reaction | ζ, Volt | Half reaction | ζ, Volt |
|---|---|---|---|
| $K^+ + e^- \rightarrow K$ | -2.936 | $2D^+ + 2e^- \rightarrow D_2$ | -0.01 |
| $Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^-$ | -1.245 | $2H^+ + 2e^- \rightarrow H_2$ | 0 |
| $2Mg(OH)_2 + 4e^- \rightarrow 2Mg + 4OH^-$ | -2.680 | | |
| $Ca^{2+} + 2e^- \rightarrow Ca$ | -2.868 | $AgBr(c) + e^- \rightarrow Ag + Br^-$ | 0.073 |
| $Na^+ + e^- \rightarrow Na$ | -2.714 | $AgCl(c) + e^- \rightarrow Ag + Cl^-$ | 0.222 |
| $Mg^{2+} + 2e^- \rightarrow Mg$ | -2.360 | $Hg_2Cl_2(c) + 2e^- \rightarrow 2Hg + 2Cl^-$ | 0.268 |
| $Al^{3+} + 3e^- \rightarrow Al$ | -1.677 | $Cu^{2+} + 2e^- \rightarrow Cu$ | 0.339 |
| $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ | -0.828 | $Cu^+ + e^- \rightarrow Cu$ | 0.518 |
| $Zn^{2+} + 2e^- \rightarrow Zn$ | -0.762 | $I_2(c) + 2e^- \rightarrow 2I^-$ | 0.535 |
| $Ga^{3+} + 3e^- \rightarrow Ga$ | -0.549 | $Hg_2SO_4(c) + 2e^- \rightarrow 2Hg + SO_4^{2-}$ | 0.615 |
| $Fe^{2+} + 2e^- \rightarrow Fe$ | -0.44 | $Fe^+ + e^- \rightarrow Fe^{2+}$ | 0.771 |
| $Cd^{2+} + 2e^- \rightarrow Cd$ | -0.402 | $Ag^+ + e^- \rightarrow Ag$ | 0.799 |
| $PbI_2(c) + 2e^- \rightarrow Pb + 2I^-$ | -0.365 | $Br_2(l) + 2e^- \rightarrow 2Br^-$ | 1.078 |
| $PbSO_4(c) + 2e^- \rightarrow Pb + SO_4^{2-}$ | -0.356 | $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$ | 1.229 |
| $Sn^{2+} + 2e^- \rightarrow Sn$ | -0.141 | $Cl_2(g) + 2e^- \rightarrow 2Cl^-$ | 1.360 |
| $Pb^{2+} + 2e^- \rightarrow Pb$ | -0.126 | $Au^+ + e^- \rightarrow Au$ | 1.69 |
| $Fe^{3+} + 3e^- \rightarrow Fe$ | -0.04 | | |

slope of regression line

$$m = \frac{\Sigma(x_i - \bar{x})(y_i - \bar{y})}{\Sigma(x_i - \bar{x})^2}$$

$$b = \bar{y} - m\bar{x}$$

Easier Form of Least Squares Equations

$$m = \frac{\Sigma x_i y_i - [(\Sigma x_i \Sigma y_i)/n]}{\Sigma x_i^2 - [(\Sigma x_i)^2/n]}$$

- n is the number of data points

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Thermodynamic properties at a standard condition (25°C and 1 bar)

| Substance | $\Delta_f H°_{298}$ ($kJmol^{-1}$) | $\Delta_f G°_{298}$ ($kJmol^{-1}$) | $S°_{m,298}$ ($Jmol^{-1}K^{-1}$) | $C_P°_{m,298}$ ($Jmol^{-1}K^{-1}$) |
|---|---|---|---|---|
| $Ag^+$ (aq) | 105.56 | 77.09 | 72.8 | - |
| Br (g) | 111.884 | 82.396 | 175.022 | 20.786 |
| $Br^+$ (aq) | -121.55 | -103.97 | 82.4 | -141.8 |
| $Br_2$ (l) | 0 | 0 | 152.231 | 75.689 |
| $Br_2$ (g) | 30.907 | 3.110 | 245.463 | 36.02 |
| C (graphite) | 0 | 0 | 5.740 | 8.527 |
| C (diamond) | 1.897 | 2.900 | 2.377 | 6.115 |
| C (g) | 716.682 | 671.257 | 158.096 | 20.838 |
| $CF_4$ (g) | -925 | -879 | 261.61 | 61.09 |
| $CH_4$ (g) | -74.81 | -50.72 | 186.264 | 35.309 |
| CO (g) | -110.525 | -137.168 | 197.674 | 29.116 |
| $CO_2$ (g) | -393.509 | -394.359 | 213.74 | 37.11 |
| $CO_3^{2-}$ (aq) | -677.14 | -527.81 | -56.9 | - |
| $COF_2$ (g) | -634.7 | -619.2 | 258.60 | 46.82 |
| $C_2H_2$ (g) | 226.73 | 209.20 | 200.94 | 43.93 |
| $C_2H_4$ (g) | 52.26 | 68.15 | 219.56 | 43.56 |
| $C_2H_6$ (g) | -84.68 | -32.82 | 229.60 | 52.63 |
| $C_2H_5OH$ (l) | -277.69 | -174.78 | 160.7 | 111.46 |
| $(CH_3)_2O$ (g) | -184.05 | -112.59 | 266.38 | 64.39 |
| $C_3H_8$ (g) | -103.85 | -23.37 | 270.02 | 73.51 |
| $C_6H_6$ (g) | 82.93 | 129.7 | 269.31 | 81.67 |
| $C_6H_{10}$ (g) | -5.36 | 107.0 | 310.86 | 105.02 |
| $C_6H_{12}O_6$ (c) | -1274.4 | -910.1 | 212.1 | 218.8 |
| $C_{12}H_{22}O_{11}$ (c) | -2221.7 | -1543.8 | 360.2 | 425.5 |
| $CH_3(CH_2)_{14}COOH$ (c) | -890.8 | -314.5 | 455.2 | 460.7 |
| $CaCO_3$ (calcite) | -1206.92 | -1128.79 | 92.9 | 81.88 |
| $CaCO_3$ (aragonite) | -1207.13 | -1127.75 | 88.7 | 81.25 |
| CaO (c) | -635.09 | -604.03 | 39.75 | 42.80 |
| Cl (g) | 121.679 | 105.680 | 165.198 | 21.840 |
| $Cl^-$ (aq) | -167.159 | -131.228 | 56.5 | -136.4 |
| $Cl_2$ (g) | 0 | 0 | 223.066 | 33.907 |
| Cu (c) | 0 | 0 | 33.150 | 24.435 |
| $Cu^{2+}$ (aq) | 64.77 | 65.49 | -99.6 | - |
| $F_2$ (g) | 0 | 0 | 202.78 | 31.30 |
| Fe (c) | 0 | 0 | 27.28 | 25.10 |
| $Fe^{3+}$ (aq) | -48.5 | -4.7 | -315.9 | - |
| H (g) | 217.965 | 203.247 | 114.713 | 20.784 |
| $H^+$ (aq) | 0 | 0 | 0 | 0 |
| $H_2$ (g) | 0 | 0 | 130.684 | 28.824 |
| HD (g) | 0.318 | -1.464 | 143.801 | 29.196 |
| $D_2$ (g) | 0 | 0 | 144.960 | 29.196 |

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| Substance | $\Delta_f H°_{298}$ ($kJmol^{-1}$) | $\Delta_f G°_{298}$ ($kJmol^{-1}$) | $S°_{m,298}$ ($Jmol^{-1}K^{-1}$) | $C_P°_{m,298}$ ($Jmol^{-1}K^{-1}$) |
|---|---|---|---|---|
| HBr (g) | -36.40 | -53.45 | 198.695 | 29.142 |
| HCl (g) | -92.307 | -95.299 | 186.908 | 29.12 |
| HF (g) | -271.1 | -273.2 | 173.779 | 29.133 |
| $HN_3$ (g) | 294.1 | 328.1 | 238.97 | 43.68 |
| $H_2O$ (l) | -285.830 | -237.129 | 69.91 | 75.291 |
| $H_2O$ (g) | -241.818 | -228.572 | 188.825 | 33.577 |
| $H_2O_2$ (l) | -187.78 | -120.35 | 109.6 | 89.1 |
| $H_2S$ (g) | -20.63 | -33.56 | 205.79 | 34.23 |
| $K^+$ (aq) | -252.38 | -283.27 | 102.5 | 21.8 |
| KCl (c) | -436.747 | -409.14 | 82.59 | 51.30 |
| Mg (c) | 0 | 0 | 32.68 | 24.89 |
| Mg (g) | 147.70 | 113.10 | 148.650 | 20.786 |
| MgO (c) | -601.70 | -569.44 | 26.94 | 37.15 |
| N (g) | 472.704 | 455.563 | 153.298 | 20.786 |
| $N_2$ (g) | 0 | 0 | 191.61 | 29.125 |
| $NH_3$ (g) | -46.11 | -16.45 | 192.45 | 35.06 |
| $NH_2CH_2COOH$ (c) | -528.10 | -368.44 | 103.51 | 99.20 |
| NO (g) | 90.25 | 86.55 | 210.761 | 29.844 |
| $NO_2$ (g) | 33.18 | 51.31 | 240.06 | 37.20 |
| $NO_3^-$ (aq) | -207.36 | -111.25 | 146.4 | -86.6 |
| $N_2O_4$ (g) | 9.16 | 97.89 | 304.29 | 77.28 |
| Na (g) | 107.32 | 76.761 | 153.712 | 20.786 |
| $Na^+$ (aq) | -240.12 | -261.905 | 59.0 | 46.4 |
| NaCl (c) | -411.153 | -384.138 | 72.13 | 50.50 |
| O (g) | 249.170 | 231.731 | 161.055 | 21.912 |
| $O_2$ (g) | 0 | 0 | 205.138 | 29.355 |
| $OH^-$ (aq) | -229.994 | -157.244 | -10.75 | -148.5 |
| $PCl_3$ (g) | -287.0 | -267.8 | 311.78 | 71.84 |
| $PCl_5$ (g) | -374.9 | -305.0 | 364.58 | 112.80 |
| $SO_2$ (g) | -296.830 | -300.194 | 248.22 | 39.87 |
| Si (g) | 455.6 | 411.3 | 167.97 | 22.251 |
| SiC (β, cubic) | -65.3 | -62.8 | 16.61 | 26.86 |
| $SiO_2$ (quartz) | -910.94 | -856.64 | 41.84 | 44.43 |
| Sn (gray) | -2.09 | 0.13 | 44.14 | 25.77 |
| Sn (white) | 0 | 0 | 51.55 | 26.99 |
| $SO_4^{2-}$ (aq) | -909.27 | -744.53 | 20.1 | -293 |