ESTIMATION OF THE SOLUBILITIES OF THE NOBLE GASES IN LIQUID METALS: PROGRAMS FOR THE HP-65 CALCULATOR AND CALCULATIONAL DETAILS

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Estimation of the Solubilities of the Noble Gases in Liquid Metals; Programs for the HP-65 Calculator and Calculational Details

by

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The present report presents details of the calculational procedure and programs for the HP-65 calculator for computing the solubilities of noble gases in liquid metals using the equations of the companion report (LBL 5159).

+ "This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, The Lawrence Berkeley Laboratory of the United States Research and Development Administration."
I. Calculation of \( p_f \equiv p_f^2 + p_f^4 \)

Program \((p_f^2, \Delta A_f^2)\) is used with the following input parameters:

\( r_g, \text{ cm}; T, \text{ K}; N_0 = 6.022 \times 10^{23}; R = 1.9872 \text{ cal/mole deg.} \) The units for pressure (cal/cm\(^3\)) were chosen for consistency with the remaining programs.

Program \((p_f^4)\) is used with the input parameters: \( r_m, \text{ cm}; r_g, \text{ cm}; C, \text{ erg cm}^6; N_0; V_m, \text{ cm}^3\text{mole}^{-1}\).

Values of \( p_f \) should be calculated at even intervals so they may be fit to a four term polynomial using Program (4 Pt). Four points are needed; the points should span the region in which \( p_f = p_c \).

II. Calculation of \( p_c (\text{cal/cm}^3) \)

Program \((\text{cavprep})\) is first used with the input parameters: \( T, \text{ K}; r_m, \text{ cm}; V_m, \text{ cm}^3\text{mole}^{-1}\). This prepares the calculator for Program \((p_cav)\) for which the input parameter is \( V_c, \text{ cm}^3\text{mole}^{-1}\). As for \( p_f \), four points are needed at even intervals and should span the region in which \( p_f = p_c \).

III. Fit of \( p_f, p_c \) to 4-term polynomials

Program (4 Pt), which is due to Brewer,\(^2\) fits \( p_f \) and \( p_c \) to the polynomials

\[
    p_f = a_0 + a_1 V_f + a_2 V_f^2 + a_3 V_f^3
    \]

\[
    p_c = b_0 + b_1 V_c + b_2 V_c^2 + b_3 V_c^3
    \]

The input parameters are: \( p_0, p_1, p_2, p_3; V_0, \text{ cm}^3/\text{mole}, \) and \( h = V_f - V_0 \).

IV. Calculation of \( V_f, \text{ cm}^3\text{mole}^{-1}\)

The polynomial for \( p_c \) is subtracted from that for \( p_f \) and the result set equal to zero. The equation \( 0 = c_0 + c_1 V + c_2 V^2 + c_3 V^3 \) is solved using Program \((V_f)\). The input parameters are: \( c_0, c_1, c_2, c_3; \) estimated values for \( V_f, \text{ cm}^3\text{mole}^{-1}\).
V. Calculation of \( p_f^0, \Delta \bar{A}_f^0 \), \( \text{cal mole}^{-1} \):

Program \( (p_f^0, \Delta \bar{A}_f^0) \) is used as in Section I, with the \( V_f \) value from Section IV.

VI. Calculation of \( p_f^1 \):

Program \( (p_f^1) \) is used as in Section II, with the \( V_f \) value from Section IV.

VII. Calculation of \( \Delta \bar{A}_f^1 \), \( \text{cal mole} \):

Program \( (\Delta \bar{A}_f^1) \) is used with the \( V_f \) of Section IV. Units for the input parameters are the same as for Program \( (p_f^1) \).

VIII. Calculation of \( \Delta \bar{G}_c \), \( \text{cal mole}^{-1} \):

Program (cavprep) is used as in Section II, followed by Program \( (\Delta \bar{G}_c - 1) \) with the input \( V_c(\equiv V_f) \), followed by Program \( (\Delta \bar{G}_c - 2) \).

IX. Calculation of \( x_g \), mole fraction gas dissolved at 1 atm gas partial pressure.

\( \Delta \bar{G}_f \) is determined from the equality

\[
\Delta \bar{G}_f = (\Delta \bar{A}_f + \Delta \bar{A}_f^1) + [(p_f^0 + p_f^1)V_f - p_g V_g]
\]

where the value of \( p_g V_g \) for the dilute gas is taken as \( p_g V_g = RT \).

The value of \( x_g \) is found using Prgm. \( (x_g) \) and the input parameters \( T \), \( (\Delta \bar{G}_f + \Delta \bar{G}_c) \), \( R \); \( V_m \), \( V_f \); the units are as previously stated.

X. Modifications

The programs are designed for a gas partial pressure of 1 atm. Henry's Law is then used to predict the solubilities at moderate pressures other than 1 atm. Program \( (p_f^0, \Delta \bar{A}_f^0) \) may be modified for \( p_g \neq 1 \) atm by replacing \( 22 \ 414 \) by \( 22 \ 414 \times p_g \), atm.

Program (cavprep) may be modified for system pressures greatly different from 1 atm by replacing 1.01325 EE6 by the system pressure in dyne cm\(^{-2} \).
Values of C (van der Waals interaction parameters) may be estimated for liquid metals using Program \((p_f^g, \Delta A_f^g)\) with \(r_g, V_f\) replaced by \(r_m, V_m\) to get \(p_m^g\); Program \((p_f^z)\) is used with \(r_g, V_f\) replaced by \(r_m, V_m\) and 
\((10^{-7} N_o C/16[4.184]V_m)\) replaced by 
\((10^{-7} N_o/16[4.184]V_m)\) to get \(p'/C_m\). 

\(C_m\) is found from the relationship 
\(p = p_m^g + p'_m\). The system pressure \(p\) is normally negligible and may be set equal to zero.

Programs \((V_f)\) and \((x_g)\) may fail on occasion if \(V_1\) or \(x_1\) is chosen too far below the desired root. This may be remedied by choosing a new value of \(V_1\) or \(x\). This has not been a problem in calculations so far carried out.

The HP-65 programs are written to be read from left to right starting at upper left hand corner.

Acknowledgment:

This work was supported by the U. S. Energy Research and Development Administration.
Program \( p_\beta^0, \Delta \rho^0 \) (calculates \( p_\beta^0 \) and \( \Delta \rho^0 \))

(2) LBL A STO2 RCL1 gx \( \times \) y \( \div \) STO3 \( \uparrow \) \( \uparrow \) X
   + 1 + RCL3 3 g \( y^x \) \( - \) 1 \( \uparrow \)
   RCL3 \( - \) 3 g \( y^x \) \( \div \) STO5 RCL6 X RCL4
   X RCL2 \( \div \) STO7 R/S
(3) RCL3 \( 4 \) X RCL3 \( \sqrt{x} \) \( -1 \) \( \sqrt{x} \) \( 3 \) X \( - \) 1
   + RCL3 \( - \) \( \sqrt{x} \) \( -1 \) \( \div \) RCL6 X RCL4 X
   STO8 2 2 4 1 4 \( \uparrow \) RCL4 X 2
   7 3 \( \bullet \) \( 1 \) \( 5 \) \( \div \) RCL2 \( \div \) \( \sqrt{x} \) LN
   RCL6 X RCL4 X \( + \) RTN 81 memory steps.

Directions:
(1) Insert tape \((p^0, \Delta \rho^0)\); \( \frac{2}{3} N_0 r_g^3 \), STO 1; T, STO 4; 1.9872, STO 6
(2) \( V_f \), A display \( p_\beta^0 \)
(3) R/S display \( \Delta \rho^0 \)

Program \( p_f^0 \) (calculates \( p_f^0 \), cal/cm\(^3\))

(2) LBL E g \( \frac{1}{x} \) RTN
   LBL A RCL8 \( \div \) 3 X \( \frac{4}{x} \) \( \div \) g \( \pi \)
   \( \div \) 3 g \( \frac{1}{x} \) g \( y^x \) STO3 RCL2 - STO4
   RCL3 RCL1 + RCL4 \( + \) STO5 RCL1 RCL2 \( + \) STO6
   RCL4 RCL6 \( \sqrt{x} \) \( -1 \) \( \sqrt{x} \) \( E \) RCL4 RCL5 \( 3 \) g
   \( y^x \) X \( \frac{4}{x} \) \( \div \) E \( - \) RCL4 RCL5 X \( \frac{1}{x} \)
   \( \sqrt{x} \) E \( + \) RCL4 \( 3 \) g \( y^x \) RCL6 X \( 2 \)
   \( \div \) E \( + \) RCL6 RCL5 \( \div \) \( r \) \( \ln \) \( 3 \) \( x \)
   RCL4 \( 4 \) g \( y^x \) \( \div \) + RCL3 \( \frac{1}{x} \) \( \sqrt{x} \) \( \div \)
   RCL7 X CHS RTN 99 memory steps.

Directions:
(1) Insert tape \((p_f^0)\); \( r_m \), STO 1; \( r_g \), STO 2; \((10^{-7} N_0 C/16 V_m[4.184])\),
   STO 7; \( N_o \), STO 8
(2) \( V_f \), A display \( p_f^0 \).
Prgm. cayprep (prepares calculator for programs (p_cay), (ΔG_i))

(2) LBL A 1 2 3 8 0 4 4 EEX
   CHS 1 6 X STO1 2 5 2 2
   5 EEX 2 4 STO 9 R/S

(3) STO3 3 g y^x RCL 9 X R/S

(4) ÷ STO2 1 0 1 3 2 5 EEX
   STO4 RCL2 1 ÷ RCL2 - ÷ STO7 f⁻¹
   √x 1 8 X STO8 RTN 61 memory steps

Directions:
(1) Insert tape (cayprep)
(2) T, A
(3) r_m, R/S
(4) V_m, R/S
(5) Leave machine on, go to tape (P_cay) or (ΔG_c-1)

Prgm. p_cay (calculates p_c; use after tape (cayprep))

(2) LBL A RCL 9 ÷ 3 g 1/x g y^x
   STO5 RCL3 + STO6 RCL8 RCL7 6 X + RCL1
   CHS X 2 ÷ RCL3 ÷ RCL3 f⁻¹ √x' RCL4
   X g π X 4 X + RCL8 RCL7 1
   2 X + RCL1 X RCL3 f⁻¹ √x ÷ 4
   ÷ RCL3 RCL4 X g π X 4 X -
   2 X RCL6 X + RCL4 4 X g π
   X RCL6 f⁻¹ √x' X + 4 ÷ 1 8
   4 EEX 7 ÷ 4 ÷ g π ÷ RCL5
   f⁻¹ √x' ÷ RTN 94 memory steps

Directions:
(1) Insert tape (p_cay)
(2) V_c, A display p_c.
Prgm. 4Pt. (Fits four evenly spaced points \((x_n, y_n)\) with \(n = 0\) to 3 to the equation \(y = b_0 + b_1 x + b_2 x^2 + b_3 x^3\)).

<table>
<thead>
<tr>
<th></th>
<th>STO1</th>
<th>STO5</th>
<th>gR+</th>
<th>gLSTx</th>
<th>STO6</th>
<th>gR+</th>
<th>gLSTx</th>
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<tbody>
<tr>
<td>3</td>
<td>÷</td>
<td>RCL5</td>
<td>+</td>
<td>RCL6</td>
<td>÷</td>
<td>2</td>
<td>÷</td>
</tr>
<tr>
<td>(g) (y^x)</td>
<td>÷</td>
<td>STO4</td>
<td>RCL8</td>
<td>RCL7</td>
<td>+</td>
<td>X</td>
<td>3</td>
</tr>
<tr>
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<td>2</td>
<td>X</td>
<td>-</td>
<td>2</td>
<td>÷</td>
</tr>
<tr>
<td>(\sqrt{x})</td>
<td>÷</td>
<td>+</td>
<td>STO3</td>
<td>RCL7</td>
<td>RCL8</td>
<td>2</td>
<td>X</td>
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<td>RCL5</td>
<td>RCL7</td>
<td>÷</td>
<td>+</td>
<td>RCL8</td>
<td>(f^{-1})</td>
<td>(\sqrt{x})</td>
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<tr>
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<td>÷</td>
<td>3</td>
<td>X</td>
<td>RCL7</td>
<td>(f^{-1})</td>
<td>(\sqrt{x})</td>
<td>+</td>
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<tr>
<td>-</td>
<td>STO2</td>
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<td>B</td>
<td>RCL1</td>
<td>2</td>
<td>X</td>
<td>-</td>
</tr>
</tbody>
</table>

(5-7) RTN RCL2 RCL3 RCL4

Directions:

1. Insert tape (4 Pt)
2, 3) \(h, \text{ STO} \); \(x_0, \text{ STO} \)
4) \(y_3, \uparrow; y_2, \uparrow; y_1, \uparrow; y_0, \text{ A display} \ b_0\)
5-7) SST display \(b_1\); SST display \(b_2\); SST display \(b_3\)
8) \(x, \text{ B display } y\)

Prgm. \(V_f\) (solves \(0 = c_0 + c_1 y + c_2 y^2 + c_3 y^3\) by successive approximation)

<table>
<thead>
<tr>
<th></th>
<th>LBL</th>
<th>D</th>
<th>STO</th>
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<th>3</th>
<th>(g) (y^x)</th>
<th>RCL8</th>
<th>X</th>
<th>RCL</th>
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<td>9</td>
<td>(f^{-1})</td>
<td>X</td>
<td>RCL7</td>
<td>X</td>
<td>+</td>
<td>RCL</td>
<td>9</td>
<td>RCL6</td>
<td>X</td>
</tr>
<tr>
<td>+</td>
<td>RCL5</td>
<td>+</td>
<td>RTN</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

(3) LBL A STO5 R/S STO6 R/S STO7 R/S STO8 RTN

Directions:

1. Insert tape \(V_f\)
2) \(c_0, A; c_1, R/S; c_2, R/S; c_3, R/S\).
3) \(V_1, \text{ D display } f(V_1); V_2, \text{ D display } f(V_2)\). \(f(V_2)\) must differ in sign from \(f(V_1)\); \(V_1 < V_2\)
4) \(V_1, \text{ STO} \text{ 1}; V_2, \text{ STO} \text{ 2 E display } V_f\)
Prgm. $\Delta A^A_1$ (calculates $\Delta A^A_1$)

(3) LBL A RCL8 $/ 3$ X $^4$ $\div$ g $\pi$
$/ 3$ g $1/x$ g $y^x$ STO3 RCL2 $-$ STO4
RCL1 + RCL3 + STO5 RCL2 + STO6 RCL4
RCL6 $/ f^{-1} \sqrt{x}$ RCL4 RCL5 $/ f^{-1} \sqrt{x}$ -
RCL4 RCL5 $/ +$ RCL4 RCL6 $/ +$ RCL5 $f$
LN - RCL6 $f$ LN + RCL7 CHS X RCL4
3 g $y^x / 4 \bullet 184$ EEX
7 $/ RTN$ 73 memory steps.

Directions:
(1) Insert tape ($\Delta A^A_1$)
(2) $r_m$, STO 1; $r_g$, STO 2; $(\pi N_0^2 c/w_m)$, STO 7; $N_0$, STO 8
(3) $V_f$, A display $-r_g$

Prgm. $G_c$ (calculates $G_c$; use after tape (cavprep))

(2) LBL A RCL 9 $/ 3$ g $1/x$ g $y^x$
STO5 RCL3 + STO6 RCL2 $/ +$ RCL2 $-$ $/$
STO7 $f^{-1} \sqrt{x}$ 1 8 X STO8 RCL7 6 X
+ RCL1 CHS X RCL3 $/ 2$ $/ +$ RCL3 $f^{-1}$
$\sqrt{x}$ RCL4 X 4 X g $\pi$ X + RCL6
X RCL8 RCL7 1 2 X + RCL1 X RCL3
$f^{-1} \sqrt{x}$ $/ 4$ $/ \div$ RCL3 RCL4 X 4 X
3 g $\pi$ X $/ -$ RCL6 $f^{-1} \sqrt{x}$ X + RTN

(4) LBL A RCL4 4 X g $\pi$ X 3 $/$
RCL6 3 g $y^x$ X + RCL8 4 $/ \div$ RCL2
RCL7 $/ f \ln -$ RCL1 X $/ +$ RCL3 3
3 g $y^x$ RCL4 X 4 X g $\pi$ X 3
$/ -$ 4 $\bullet 184$ EEX 7 $/$
6 $\bullet 0 2 2$ EEX 2 $/ 3 X$ RTN

80 memory steps.

R 1 2 3 4 5 6 7 8

$2 \Delta A^A_1$ memory steps.

$\gamma_m$ $r_m$ $r_c$ $r_c-r_g$ $2r_c+r_m$ $r_m+r_g$ $\frac{\pi N_0^2 c}{w_m}$ $N_0$

--7--

cont'd. on pg. 8
cont'd from page 7

**Directions:**

1. Insert tape $(\Delta \bar{C}_c - 1)$
2. $V_c, A$
3. Insert tape $(\Delta \bar{C}_c - 2)$
4. A display $\Delta \bar{C}_c$

---

**Prog. $x_g$ (calculates $x_g$ by successive approximation)**

<table>
<thead>
<tr>
<th>(3) LBL D STO4 RCL8 X 1 RCL4 - RCL7 X + STO 9 RCL4 RCL8 X RCL 9 ÷ f</th>
<th>(4) LBL E RCL2 D STO3 g ABS 1 gx&gt;y RCL2 RTN RCL1 D ÷ ÷ RCL3 - RCL2 RCL1 - gx&gt;y ÷ X g ABS RCL1 + STO2 GTO E</th>
</tr>
</thead>
</table>

88 memory steps.

| R 1 2 3 4 5 6 7 8 9 |
| x₁ x₂ f(x₂) x₉ (Δ\bar{C}_f+Δ\bar{C}_c) RT V₉ V₉ used in D |

---

**Directions:**

1. Insert tape $x_g$
2. $(Δ\bar{C}_f+Δ\bar{C}_c), A; T, R/S; V_m, R/S; V_r, R/S.$
3. $x_1, D$ display $f(x_1); x_2, D$ display $f(x_2). f(x_1)$ and $f(x_2)$ must have opposite sign; $x_1 < x_2.$
4. $x₁, STO 1; x₂, STO 2 E$ display $x_g.$
References


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