Solutions Manual to Accompany

Physical Chemistry

by Joseph H. Noggle
John M. Pope
Juliana G. Serafin

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Little, Brown and Compan
Boston Toronto

ISBN 0-316-61165-4

9 8 7 6 5 4 3 2

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Published simultaneously in Canada
by Little, Brown & Company (Canada) Limited

Printed in the United States of America

Preface

This Solutions Manual is intended to help students of physical chemistry become proficient at problem solving. To obtain the most benefit from this manual, we encourage you to proceed as follows:

1. Read relevant section(s) in the text.
2. Attempt to solve the problems without using the solutions manual.
3. Reread the text section.
4. Use the solutions manual.

Some obvious steps, such as unit conversions, have been left out of the problem solutions. We hope that this will not cause any confusion.

We will be glad to hear of any mistakes found by the reader. These may be sent to J. Pope and J. Serafin, in care of Science Editor, College Division, Little, Brown and Company.

We would like to thank Professor Joseph Noggle for his valuable comments and Ron Pullins and Sally Stickney for their help.

J.M. Pope
J.G. Serafin

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Problems

1.1 Dry air is roughly 79% N_2 and 21% O_2. Calculate its average molecular weight and density at STP using the ideal gas law.

$\bar{M}_{air}$ = average molecular weight = $0.79\, M_{N_2} + 0.21\, M_{O_2}$

$\bar{M}_{air} = 0.79\,(28.013\,g) + 0.21\,(31.999\,g) = 28.85\,g.$

The density is given by eqn (1.1c)

$$\rho = \frac{P\bar{M}}{RT} = \frac{(101325\,Pa)(28.85\,g)}{(8.3143\,JK^{-1})(273.15\,K)} = 1287.2\,g\,m^{-3} \text{ or}$$

$$\rho = 0.001287\,g\,cm^{-3}$$

1.2 Use the van der Waals equation to calculate the pressure exerted by SO_2 at 500 K if the density is 100 g/dm^3.

From eqns. (1.1b) and (1.1c), $V_m = \frac{M}{\rho} = \frac{64.06\,g}{100\,g\,dm^{-3}} = 0.64\,dm^3.$

The van der Waals eqn (1.3) is

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{(.08206\ dm^3 atm/K)(500\ K)}{(.64\ dm^3 - .0564\ dm^3)} - \frac{(6.71\ dm^6 atm)}{(.64\ dm^3)^2} \quad \text{or}$$

$P = 53.9$ atm.

1.3 Calculate the molecular diameter (σ) of CO_2 from its van der Waals constant.

From eqn (1.4), $\sigma = \left(\frac{3b}{2\pi L}\right)^{1/3}$. Using data from Table 1.1,

$$\sigma = \left(\frac{3(.0427\ dm^3)}{2\pi(6.02217 \times 10^{23})}\right)^{1/3} = 3.23 \times 10^{-9}\ dm = 3.23 \times 10^{-8}\ cm.$$

1.4 Calculate the pressure exerted by 3.00 moles of CO_2 in a 9.00-dm^3 container at 400 K using (a) ideal gas, (b) van der Waals. (c) Repeat the calculation for a volume of 2.00 dm^3.

a) From the ideal gas law, $P = \frac{nRT}{V}$ or

$$P = \frac{(3.0)(.08206\ dm^3 atm K^{-1})(400\ K)}{(9.0\ dm^3)} = 10.94\ atm.$$

b) From eqn (1.3), $P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$ or

$$P = \frac{(3.0)(.08206\ dm^3 atm\ K^{-1})(400\ K)}{9\ dm^3 - (3.0)(.0427\ dm^3)} - \frac{(3.0)^2(3.59\ dm^6 atm)}{(9.0\ dm^3)^2} = 10.70\ atm$$

c) With $V = 2.00$ dm^3, Ideal Gas Law : $P = 49.23$ atm,

van der Waals : $P = 44.53$ atm.

1.5 Use the Dieterici equation to calculate the pressure exerted by 3.00 moles of CO_2 at 400 K in a container with volume (a) 9.00 dm^3, (b) 2.00 dm^3.

From eqn (1.6), $P = \frac{RT}{V_m - b} \exp\left(\frac{-a}{RTV_m}\right)$.

a) Using Table 1.1 and $V_m = 3.00$ dm^3,

$$P = \frac{(.08206\ dm^3 atm K^{-1})(400 K)}{(3.00\ dm^3 - .0463\ dm^3)} \exp\left(-\frac{4.621}{(.08206)(400)(3.00)}\right) = 10.60\ atm.$$

b) With $V_m = 2/3$ dm^3, $P = 42.84$ atm.

1.6 Calculate the molar volume of CH_4 at 298 K and 10.0 atm using (a) ideal gas, (b) van der Waals equation of state.

a) From eqn (1.1b), $V_m = \frac{RT}{P} = \frac{(.08206\ \text{dm}^3\text{atm K}^{-1})(298\text{K})}{(10\ \text{atm})} = 2.445\ \text{dm}^3$.

b) Start with eqn (1.9), $V_m = \frac{RT}{P + (a/V_m^2)} + b$. Use the ideal gas solution from part a) to find the right-hand side and continue iterating: $V_m^{(1)} = 2.445\ \text{dm}^3$, $V_m^{(2)} = 2.399\ \text{dm}^3$, $V_m^{(3)} = 2.396\ \text{dm}^3$, $V_m^{(4)} = 2.396\ \text{dm}^3$.

1.7 Use the van der Waals equation to calculate the volume occupied by 5.00 moles of NH_3 at 300 K, 7.00 atm.

Same method as in 1.6 b). From the ideal gas law, $V^{(1)} = \frac{nRT}{P} = 17.58\ \text{dm}^3$. Iterate to find $V^{(4)} = 16.90\ \text{dm}^3$.

1.8 Show that the Dieterici equation is nearly identical to the van der Waals equation at high temperatures or low densities (i.e., when $a/RTV_m << 1$).

Expand eqn.(1.6) in a Taylor series:

$$P = \frac{RT}{V_m - b}\left[1 - \frac{a}{RTV_m} + \frac{1}{2}\left(\frac{a}{RTV_m}\right)^2 + \ldots\right].$$ If $\frac{a}{RTV_m} << 1$,

$$P \cong \frac{RT}{V_m - b} - \frac{a}{(V_m - b)V_m}.$$ The van der Waals eqn. is

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2},$$ which is nearly identical to the above.

1.9 The data below for acetylene at 25°C give the PV product divided by P_0V_0 (at 0°C and 1 atm). Use a graphical or least-squares method to determine P_0V_0 and the second virial coefficient at this temperature.

P (atm)	(PV/P_0V_0)	P (atm)	(PV/P_0V_0)
0.5	1.0989	6	1.0531
1	1.0937	8	1.0385
2	1.0841	10	1.0255
4	1.0684	12	1.0139

From eqn (1.13), $PV \cong RT + BP$. Dividing by P_0V_0 gives $\frac{PV}{P_0V_0} = \frac{RT}{P_0V_0} + P\left(\frac{B}{P_0V_0}\right)$. Regressing $\frac{PV}{P_0V_0}$ vs. P yields

slope $= \frac{B}{P_0V_0} = -7.4227 \times 10^{-3} \pm 2.0258 \times 10^{-4}$ and

intercept $= \frac{RT}{P_0V_0} = 1.0999 \pm .0014$. Then $P_0V_0 = 22.243$ dm³atm

and $B = -0.165$ dm³.

1.10 Use the measured compressibility factors given below for methane at 203 K to calculate the second virial coefficient. You could also get an estimate of the third virial coefficient (C) from these data.

P (atm)	z
1	0.9940
10	0.9370
20	0.8683
30	0.7928

From eqns (1.10) and (1.11), $V_m(z-1) = B + \frac{C}{V_m}$ with $V_m = \frac{zRT}{P}$.
A plot of $V_m(z-1)$ vs. $\frac{1}{V_m}$ gives slope $= C = .004$ dm⁶ and intercept $= B = -.100$ dm³.

1.11 The virial coefficients [for Eq. (1.13)] of hydrogen at 223 K are given below (PV in dm³ atm); use them to calculate the compressibility of this gas at 50 atm.

$B = 1.2027 \times 10^{-2}$, $\delta = -1.741 \times 10^{-8}$

$\gamma = 1.164 \times 10^{-5}$, $\varepsilon = 1.022 \times 10^{-11}$

Rearrange eqn (1.13) to $z = 1 + \frac{BP}{RT} + \frac{\gamma P^2}{RT} + \frac{\delta P^3}{RT} + \frac{\varepsilon P^4}{RT}$. Plugging in the data, $z = 1.0343$.

1.12 Calculate the second virial coefficient of N_2 at 473.15 K using (a) van der Waals, (b) Beattie-Bridgeman, (c) Berthelot equations. The observed value is 14.76 cm^3.

a) From eqn (1.18), $B = b - \frac{a}{RT}$. Using the data of Table 1.1, $B = 3.3\ cm^3$ for N_2.

b) From eqn (1.16), $B = B_0 - \frac{A_0}{RT} - \frac{c}{T^3}$. Using the data of Table 1.2, $B = 15.4\ cm^3$.

c) From eqn. (1.17), $B = \frac{9RT_c}{128P_c}\left(1 - \frac{6T_c^2}{T^2}\right)$. Using the data from Table 1.1, $B = 0.0125\ dm^3 = 12.5\ cm^3$.

1.13 Calculate the Boyle temperature of argon using (a) van der Waals and (b) Berthelot forms of the second virial coefficient. (c) Use the Beattie-Bridgeman form of the second virial coefficient to calculate the Boyle temperature of argon. The actual value is 410 K.

a) From eqn (1.18), $T_B = \frac{a}{bR}$. Using the data of Table 1.1 $T_B = 509\ K$.

b) From eqn (1.17), $T_B = \sqrt{6}\,T_c$. Thus $T_B = 370\ K$.

c) Setting $B(T_B) = 0$, $B(T_B) = B_0 - \frac{A_0}{RT_B} - \frac{C}{T_B^3} = 0$ and $T_B^3 - \left(\frac{A_0}{RB_0}\right)T_B^2 - \frac{C}{B_0} = 0$. Using Table 1.2,

$T_B^3 - 400.12\ T_B^2 - 1.5238 \times 10^6\ K^3 = 0$. The solution is (see Appendix I of text) $T_B = 409\ K$.

1.14 Calculate the Boyle temperature of He using the (a) van der Waals, (b) Berthelot, (c) Beattie-Bridgeman forms for $B(T)$.

a) Same method as 1.13a, $T_B = 17$ K.

b) Same method as 1.13a, $T_B = 13$ K.

c) Same method as 1.13a, $T_B = 24$ K.

1.15 Derive an expression for the second virial coefficient of a gas in terms of the Dieterici constants from Eq. (1.6).

Multiply eqn (1.6) by $\frac{V_m}{RT}$ to get $z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} \exp\left(\frac{-a}{RTV_m}\right)$.

Expanding the exponential in a Taylor series,

$z = \frac{V_m}{V_m - b}\left(1 - \frac{a}{RTV_m} + \frac{1}{2}\left(\frac{a}{RTV_m}\right)^2 + \ldots\right)$. Also

$\frac{V_m}{V_m - b} = \frac{1}{1 - b/V_m} = \left(1 + b/V_m + (b/V_m)^2 + \ldots\right)$. Thus

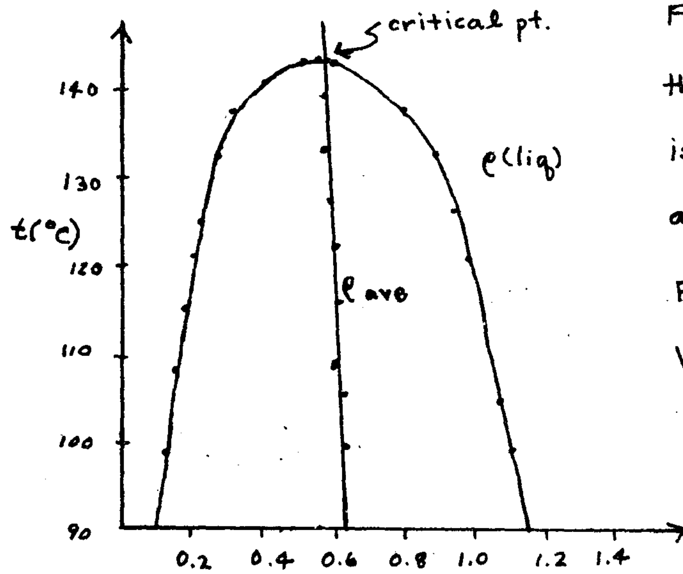
$z = \left(1 + \frac{b}{V_m} + \ldots\right)\left(1 - \frac{a}{RTV_m} + \ldots\right) = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} - \left(\frac{ab}{RT}\right)\frac{1}{V_m^2} + \ldots$

Comparison to eqn (1.11) shows $B = b - \frac{a}{RT}$.

1.16 Use the data below to determine the critical constants of Cl_2.

t (°C)	Liquid density (g/cm^3)	Vapor density (g/cm^3)
98.9	1.115	0.124
104.4	1.087	0.139
110.0	1.057	0.156
115.6	1.025	0.179
121.1	0.989	0.203
126.7	0.949	0.231
132.2	0.894	0.268
137.8	0.814	0.321
143.3	0.599	0.523

Use the method illustrated in Figure 1.4. Calculate $\rho_{avg} = \frac{1}{2}(\rho_{liq} + \rho_{vap})$ and make the following plot



From the plot, the critical point is at $t_c = 144°C$ and $\rho_c = 0.57\ g/cm^3$.
For Cl_2, $M = 70.906\ g$
$V_c = \frac{M}{\rho_c} = 124\ cm^3$.

1.17 Use the Berthelot equation (1.5) at the critical point to derive relationships between the critical constants and the constants a and b.

For eqn (1.5) at the critical point, $P = \frac{RT_c}{V_c - b} - \frac{a}{T_c V_c^2}$.

$$\frac{\partial P_c}{\partial V_c} = \frac{-RT_c}{(V_c-b)^2} + \frac{2a}{T_c V_c^3} = 0 \ , \ \frac{\partial^2 P_c}{\partial V_c^2} = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{T_c V_c^4} = 0.$$

We combine the last two equations to find $V_c = 3b$.
Substitute this into $\frac{\partial P_c}{\partial V_c}$ to find $T_c = \sqrt{8a/27Rb}$.
Substitute this and $V_c = 3b$ into the expression for P_c,
$P_c = \sqrt{\frac{Ra}{216 b^3}}$.

1.18 Use the law of corresponding states (Fig. 1.10) to calculate the molar volume of NO at 165 K and 19.5 atm.

From Table 1.1, we have for NO

$$T_r = \frac{T}{T_c} = \frac{165}{183} = 0.902 \ , \ P_r = \frac{P}{P_c} = \frac{19.5}{65} = 0.300.$$

From the "low pressure region" part of Figure 1.10 we find $z = \frac{PV_m}{RT} = 0.83$ so $V_m = \frac{0.83\,RT}{P} = .58\ dm^3$.

1.19 Silicon tetrafluoride (SiF_4) has a critical temperature 259.1 K and critical pressure 36.7 atm. Calculate the van der Waals constants; then use the van der Waals equation to calculate the vapor density of this gas at STP.

From Table 1.4, the van der Waals constants are

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{27(.08206\ dm^3atm/K)^2(259.1\ K)^2}{64(36.7\ atm)} = 5.197\ dm^6atm$$

$$b = \frac{RT_c}{8P_c} = \frac{(.08206\ dm^3atm/K)(259.1\ K)}{8\ (36.7\ atm)} = 0.0724\ dm^3$$

Calculating the molar volume with eqn (1.9) as in problem 1.6 b) with the first $V_m = \frac{RT}{P}$, $V_m^{(1)} = 22.415\ dm^3$, $V_m^{(2)} = 22.258\ dm^3$, $V_m^{(3)} = 22.254\ dm^3$ and $V_m^{(4)} = 22.254\ dm^3$.

The density is $\rho = \frac{M}{V} = \frac{104.079\ g}{22.254\ dm^3} = 4.679\ g/dm^3$.

1.20 (a) Calculate the Dieterici constants of methane from the critical constants.
(b) Use these constants to calculate the pressure of methane when $T = 270$ K, $V_m = 0.1\ dm^3$.
(c) Use successive approximations and the Dieterici equation to calculate V_m when $P = 10$ atm and $T = 270$ K.

a) From Table 1.4, the Dieterici constants are

$$a = \frac{4R^2T_c^2}{e^2P_c} = \frac{4(.08206\ atm dm^3/K)^2(190.6\ K)^2}{e^2(45.8\ dm^3)} = 2.891\ dm^6atm$$

$$b = \frac{RT_c}{e^2P_c} = \frac{(.08206\ atm dm^3/K)(190.6\ K)}{e^2(45.8\ dm^3)} = 0.04622\ dm^3$$

b) From eqn (1.6), $P = \frac{RT}{V_m - b}\exp\left(\frac{-a}{RT\,V_m}\right) = 111.7$ atm

c) Rewriting eqn (1.6) as $V_m = \frac{RT}{P}\exp\left(\frac{-a}{RTV_m}\right) + b$, we solve this as we did in problem 1.6 b), with $V_m^{(1)} = \frac{RT}{P} = 2.216\text{dm}^3$ as a first approximation. Then $V_m^{(2)} = 2.135\text{ dm}^3$, $V_m^{(3)} = 2.130\text{ dm}^3$, $V_m^{(4)} = 2.130\text{ dm}^3$.

1.21 Calculate the number density n^* of an ideal gas at 298 K and 1 atm.

From eqn (1.22b), the number density is

$$n^* = \frac{PL}{RT} = \frac{(1\text{ atm})(6.02217\times10^{23})}{(.08206\text{ atm dm}^3/\text{K})(298\text{ K})} = 2.463\times10^{19}\text{cm}^{-3}.$$

1.22 Calculate the number of collisions which hydrogen molecules would make with 1 cm^2 of a wall in one second at 150 K and a pressure of (a) 1 torr, (b) 1 atm.

a) From eqn (1.22b), $n^* = \frac{PL}{RT} = \frac{(\frac{1}{760}\text{ atm})(6.02217\times10^{23})}{(.08206\text{ atm dm}^3/\text{K})(150\text{ K})}$

$n^* = 6.437\times10^{16}\text{cm}^{-3}$. From eqn (1.33),

$$z_{wall} = n^*\left(\frac{RT}{2\pi M}\right)^{1/2} = (6.437\times10^{16}/\text{cm}^3)\left(\frac{8.3143\times10^7\text{erg/K}(150\text{ K})}{2\pi(2.016\text{ g})}\right)^{1/2}$$

$z_{wall} = 2.02\times10^{21}\text{cm}^{-2}\text{s}^{-1}$.

b) At $P = 1$ atm, $n^* = 4.892\times10^{19}\text{cm}^{-3}$, $z_{wall} = 1.54\times10^{24}\text{cm}^{-2}\text{s}^{-1}$.

1.23 In a Knudsen experiment, a substance with a molecular weight of 0.210 kg is placed in a cell with a hole of area $3\times10^{-6}\text{ m}^2$. At 500 K, the weight lost in 10 minutes is 30 mg. Calculate the vapor pressure of this substance.

We start with $\mu = \frac{\Delta W}{A}\Delta t = \frac{(3\times10^{-5}\text{kg})}{(3\times10^{-5}\text{m}^3)}(600\text{ s}) = 1.667\times10^{-3}$

From eqn (1.34), the vapor pressure is

$$P = \mu\left(\frac{2\pi RT}{M}\right)^{1/2} = (1.667\times10^{-3})\left(\frac{2\pi(8.3143\text{ J/K})(500\text{ K})}{.210\text{ kg}}\right)^{1/2} = 5.80\times10^{-6}\text{atm}.$$

1.24 Derive a formula for the speed distribution of a two-dimensional gas. This has application in the study of adsorbed species which may have freedom of motion about the surface of the adsorbent.

Proceed as in 3 dimensions; $f(v_x, v_y) = a^2 e^{-bv_x^2} e^{-bv_y^2} = a^2 e^{-bv^2}$ where $a = \sqrt{\frac{m}{2\pi kT}}$, $b = \frac{m}{2kT}$. Points in velocity space with speeds between v and $v+dv$ will lie within a ring of area $A = 2\pi v dv$, thus

$$f(v)dv = a^2 e^{-bv^2} 2\pi v dv = \frac{mv}{kT} \exp\left(\frac{-mv^2}{2kT}\right) dv$$ in 2-D space.

1.25 Calculate the average and rms speeds of N_2 at 500°C.

From eqn (1.38), the average speed is

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.3143\ J/K)(773.15\ K)}{\pi(.0280\ kg)}} = 764\ m/s.$$

From eqn (1.28),

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.3143\ J/K)(773.15\ K)}{(.0280\ kg)}} = 830\ m/s.$$

1.26* Calculate the average, rms, and most probable speeds for CO_2 at 300 K.

From eqn (1.38), $\bar{v} = \sqrt{\frac{8RT}{\pi M}} = \left(\frac{8(8.3143\ J/K)(300\ K)}{\pi(.04401\ kg)}\right)^{1/2} = 380\ m/s$

From eqn (1.28), $u = \sqrt{\frac{3RT}{M}} = \left(\frac{3(8.3143\ J/K)(300\ K)}{(.04401\ kg)}\right)^{1/2} = 412\ m/s$

$$v_p = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.3143\ J/K)(300\ K)}{(.04401\ kg)}} = 337\ m/s$$

1.27 Calculate the fraction of molecules in a gas which have velocities greater than $3v_p$. The required integral can be done numerically (Appendix I); it will be sufficiently accurate to use five steps for $3 < (v/v_p) < 3.5$ and five steps for $3.5 < (v/v_p) < 4.5$; above 4.5 the contribution is insignificant.

The fraction of molecules with speeds in a given interval is $P(V_1 \text{ to } V_2) = \frac{4}{\sqrt{\pi}}\int_{\omega_1}^{\omega_2} e^{-\omega^2}\omega^2 d\omega$, eqn (1.40b), where $\omega = V/V_p$. For the interval from $\omega_1 = 3V_p$ to $\omega_2 = \infty$: $P = \frac{4}{\sqrt{\pi}}\int_3^{\infty} e^{-\omega^2}\omega^2 d\omega$. A numerical solution (Appendix I, Simpson's Rule) gives $P = 440$ ppm.

1.28 Calculate the fraction of molecules in a gas which has a kinetic energy greater than $10kT$.

A molecule with kinetic energy $E = 10\,kT = \frac{1}{2}mV_0^2$ has $V_0 = \sqrt{\frac{20kT}{m}}$. The fraction of molecules with $V > V_0$ is given by eqn (1.40b), $P(V > V_0) = \frac{4}{\sqrt{\pi}}\int_{\omega_0}^{\infty} e^{-\omega^2}\omega^2 d\omega$ where $\omega_0 = V/V_p = \frac{\sqrt{\frac{20kT}{m}}}{\sqrt{\frac{2kT}{m}}} = \sqrt{10}$. Thus from numerical integration (App. I, Simpson's Rule) $P(V>V_0) = 1.7 \times 10^{-4}$.

1.29 Find the distance r/σ at which the Lennard-Jones potential $U(r)$ is a minimum. Show that the value of $U(r)$ at the minimum is $-\varepsilon$.

$V(r)$ is a minimum when $\frac{dV(r)}{dr} = 0$. From eqn (1.43), $V(r) = 4\varepsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right)$: $\frac{dV(r)}{dr} = 4\varepsilon\left(-\frac{12\sigma^{12}}{r_m^{13}} + \frac{6\sigma^6}{r_m^7}\right) = 0$. Thus $r_{min} = 2^{1/6}\sigma$. It is easily verified that $\frac{d^2V}{dr^2} > 0$, so r is a minimum. Then $V(r_m) = 4\varepsilon\left[\frac{1}{4} - \frac{1}{2}\right] = -\varepsilon$.

1.30 Calculate the third virial coefficient (C) of CO at 300 K from its Lennard-Jones constants (Table 1.7).

From eqn (1.45) and Table 1.7, $T^* = \frac{T}{(\varepsilon/k)} = \frac{300\text{K}}{100.2\text{ K}} = 2.994$.
From Figure 1.22, we read $C^* = 0.35$. From eqn (1.48),
$C = b_0^2 C^*$, $C = 1.6 \times 10^{-3} \text{dm}^6$.

1.31 Derive a formula for the second virial coefficient from the Sutherland potential with $n = 6$. Assume $\epsilon/kT < 1$ so that the exponential can be expanded with $e^x = 1 + x + x^2/2 + x^3/6 + \cdots$ (keep exactly that number of terms).

The Sutherland potential is $\begin{cases} u = \infty & 0 < r < \sigma \\ u = -\varepsilon\left(\frac{\sigma}{r}\right)^6 & \sigma < r < \infty \end{cases}$.

Using eqn (1.41) over 2 regions of integration
$B(T) = 2\pi L\left[\int_0^\sigma r^2 dr + \int_\sigma^\infty (1 - e^{-u/kT})r^2 dr\right]$. The first integral is $2\pi L \int_0^\sigma r^2 dr = \frac{2}{3}\pi L\sigma^3 = b_0$. Expanding the exponential of the second integral

$$2\pi L\int_\sigma^\infty (1-e^{-u/kT})r^2 dr = -2\pi L\int_\sigma^\infty\left(\frac{\varepsilon\sigma^6}{r^4 kT} + \frac{1}{2}\frac{\varepsilon^2\sigma^{12}}{r^{10}(kT)^2} + \frac{1}{6}\frac{\varepsilon^3\sigma^{18}}{r^{16}(kT)^3} + \ldots\right)dr$$

$$= -b_0\left(\frac{\varepsilon}{kT} + \frac{1}{6}\left(\frac{\varepsilon}{kT}\right)^2 + \frac{1}{30}\left(\frac{\varepsilon}{kT}\right)^3 + \ldots\right)$$

thus $B(T) = b_0\left(1 - \frac{\varepsilon}{kT} - \frac{1}{6}\left(\frac{\varepsilon}{kT}\right)^2 - \frac{1}{30}\left(\frac{\varepsilon}{kT}\right)^3 + \ldots\right)$

1.32 Derive Eq. (1.49) for the second virial coefficient of a gas with a square-well potential.

The square well potential is $\begin{cases} u = \infty & 0 < r < \sigma \\ u = -\varepsilon & \sigma < r < R\sigma \\ u = 0 & R\sigma < r < \infty \end{cases}$

Proceeding as in problem 1.31, eqn (1.41) gives