

PART ONE

THERMODYNAMICS

CHAPTER 1: First Law of Thermodynamics

- ✓ 1.1 Assuming that the atmosphere is isothermal at 0 °C and that the average molar mass of air is 29 g mol⁻¹, calculate the atmospheric pressure at 20,000 ft above sea level.

SOLUTION

$$h = (2.0 \times 10^4 \text{ ft})(12 \text{ in ft}^{-1})(2.54 \text{ cm in}^{-1})(10^{-2} \text{ m cm}^{-1})$$

$$= 6096 \text{ m}$$

$$P = P_0 e^{-gMh/RT}$$

$$P = (1.013 \text{ bar}) \exp \left[\frac{-(9.8 \text{ m s}^{-2})(29 \times 10^{-3} \text{ kg mol}^{-1})(6096 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273 \text{ K})} \right]$$

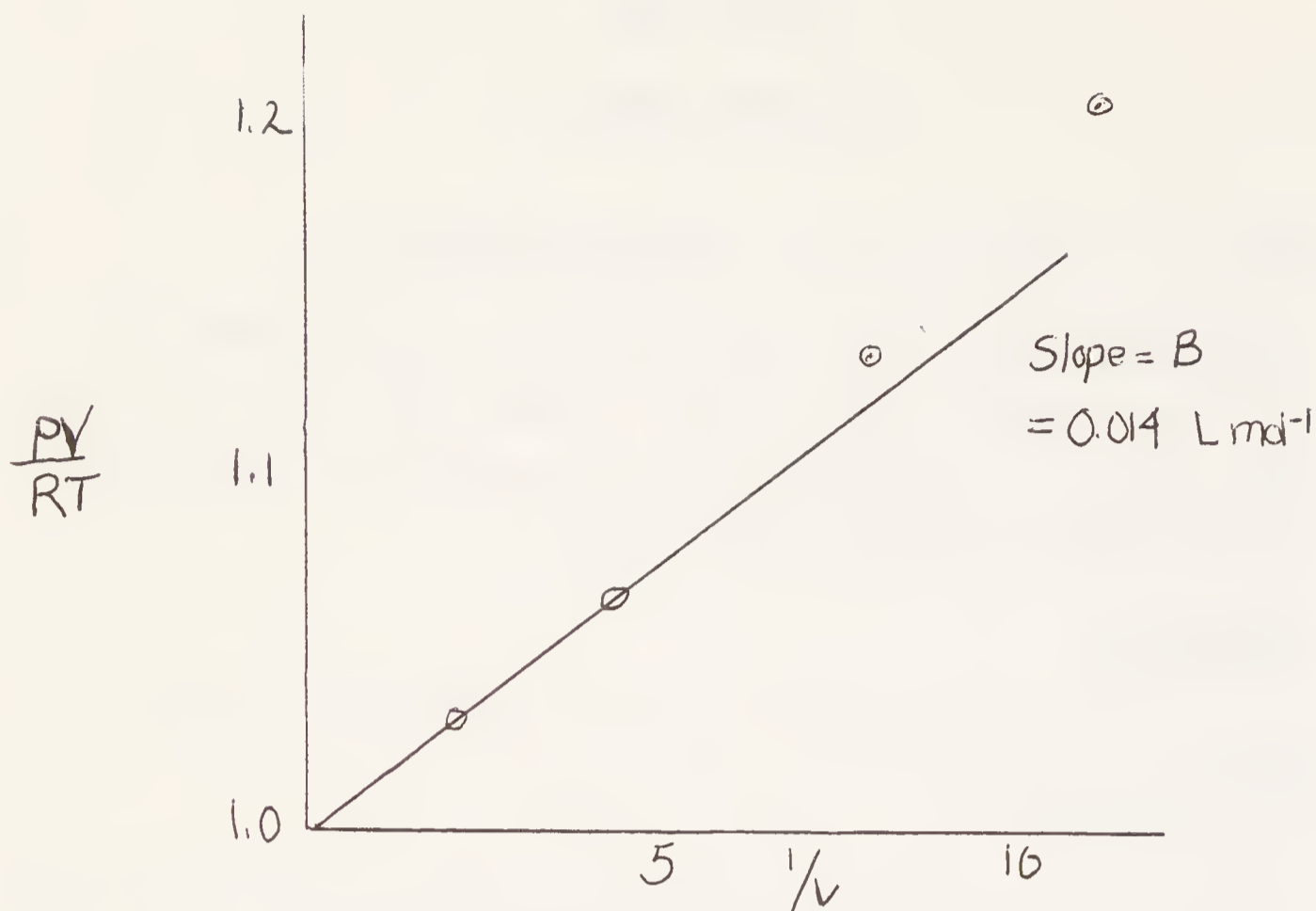
$$= 0.472 \text{ bar}$$

- ✓ 1.2 Calculate the second virial coefficient of hydrogen at 0 °C from the fact that the molar volumes at 50.7, 101.3, 202.6, and 303.9 bar are 0.4634, 0.2386, 0.1271, and 0.09004 L mol⁻¹, respectively.

SOLUTION

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$

P/bar	50.7	101.3	202.6	303.9
V/L mol ⁻¹	0.4634	0.2386	0.1271	0.09004
PV/RT	1.035	1.064	1.134	1.205
(1/V)/mol L ⁻¹	2.158	4.191	7.868	11.106



- ✓ 1.3 The second virial coefficient B of methyl isobutyl ketone is $-1580 \text{ cm}^3 \text{ mol}^{-1}$ at 120°C . Compare its compressibility factor at this temperature with that of a perfect gas at 1 bar.

SOLUTION
$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} = 1 + \frac{BP}{RT}$$

In the B/V term, V may be replaced by RT/P if $Z \approx 1$, since the approximation is made in a small correction term. At 1 atm

$$Z = 1 + \frac{(-1.58 \text{ L mol}^{-1})(1 \text{ bar})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(393.15 \text{ K})}$$

$$= 0.952$$

The compressibility factor for a perfect gas is of course unity.

- ? 1.4 Using Fig. 1.4 calculate the compressibility factor Z for $\text{NH}_3(\text{g})$ at 400 K and 50 bar.

SOLUTION
$$B = -110 \text{ cm}^3 \text{ mol}^{-1}$$

$$B' = \frac{B}{RT} = \frac{-(110 \text{ cm}^3 \text{ mol}^{-1})(10^{-3} \text{ L cm}^{-3})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(400 \text{ K})}$$

$$= -3.31 \times 10^{-3} \text{ bar}^{-1}$$

$$Z = 1 + B'P = 1 - (3.31 \times 10^{-3} \text{ bar}^{-1})(50 \text{ bar})$$

$$= 0.835$$

7. 1.5 Show that the virial equation written in terms of pressure has the following form for a van der Waals gas
- $$Z = 1 + [b - (a/RT)](P/RT)$$
- if terms in P^2 , P^3 , etc., are neglected.

SOLUTION

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{VRT}$$

Adding and subtracting $\frac{V-b}{V-b}$ on the right side of the equation

$$\frac{PV}{RT} = 1 + \frac{b}{V-b} - \frac{a}{VRT}$$

Since the second and third terms are small correction terms, b can be ignored in comparison with V ; and V in the second and third term can be replaced by RT/P .

$$Z = 1 + \frac{bP}{RT} - \frac{aP}{(RT)^2} = 1 + \left[b - \frac{a}{RT} \right] \left[\frac{P}{RT} \right]$$

- 1.6 Show that for a gas of spherical molecules b in the van der Waals equation is four times the molecular volume times Avogadro's constant.

SOLUTION

The molecular volume for a spherical molecule is

$$\frac{4}{3}\pi \left(\frac{d}{2}\right)^3 = \frac{\pi}{6}d^3$$

where d is the diameter. Since the center of a second spherical molecule cannot come within a distance d of the center of the first spherical molecule, the excluded volume per pair of molecules is

$$\frac{4}{3} \pi d^3$$

The constant b in van der Waals equation is the excluded volume per molecule times Avogadro's constant

$$b = \frac{2}{3} \pi d^3 N_A = 4 \left(\frac{\pi}{6} d^3 \right) N_A$$

- ✓ 1.7 How much work is done when a person weighing 75 kg (165 lbs.) climbs the Washington monument, 555 ft high? How many kilojoules must be supplied to do this muscular work, assuming that 25% of the energy produced by the oxidation of food in the body can be converted into muscular mechanical work?

SOLUTION

$$w = mgh$$

$$\begin{aligned} \text{work} &= (\text{mass})(\text{acceleration of gravity})(\text{height}) \\ &= (75\text{kg})(9.806\text{m s}^{-2})(555\text{ft}) \times (12\text{in ft}^{-1}) \times \\ &\quad (2.54 \times 10^{-2}\text{m in}^{-1}) \\ &= 1.244 \times 10^5 \text{ J} \end{aligned}$$

The energy needed is four times greater than the work done.

$$\begin{aligned} E &= 4 (1.244 \times 10^5 \text{ J}) \\ &= 497.6 \text{ kJ} \end{aligned}$$

- ✓ 1.8 Derive the expression for the reversible isothermal work for a van der Waals gas.

SOLUTION

$$w = - \int_{V_1}^{V_2} P dV \quad P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$w = - \int_{V_1}^{V_2} \frac{RT}{v-b} dV \quad + \quad \int_{V_1}^{V_2} \frac{a}{V^2} dV$$

$$= - RT \ln \frac{V_2-b}{V_1-b} + a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

✓ 1.9 Are the following expressions exact differentials?

(a) $xy^2 dx - x^2 y dy$ (b) $\frac{dx}{y} - \frac{x}{y^2} dy$

SOLUTION

(a) Taking the cross derivatives

$$\frac{\partial xy^2}{\partial y} = 2xy \quad \frac{\partial (-x^2 y)}{\partial x} = -2xy$$

Since the cross derivatives are unequal, the expression is not an exact differential.

(b) $\frac{\partial (1/y)}{\partial y} = -\frac{1}{y^2} \quad \frac{\partial (-x/y^2)}{\partial x} = -\frac{1}{y^2}$

Since the cross derivatives are equal, the expression is an exact differential.

1.10 A mole of liquid water is vaporized at 100 °C and 1.013 bar. The heat of vaporization is 40.69 kJ mol⁻¹. What are the values of (a) w_{rev} , (b) q , (c) ΔU , and (d) ΔH ?

SOLUTION

(a) Assuming that water vapor is a perfect gas and that the volume of liquid water

is negligible,

$$\begin{aligned} w &= -P\Delta V = -RT \\ &= -(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(373.15 \text{ K}) \\ &= -3.10 \text{ kJ mol}^{-1} \end{aligned}$$

(b) The heat of vaporization is $40.69 \text{ kJ mol}^{-1}$, and, since heat is absorbed, q has a positive sign.

$$q = 40.69 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \text{(c) } \Delta U &= q + w \\ &= (40.69 - 3.10) \text{ kJ mol}^{-1} \\ &= 37.59 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(d) } \Delta H &= \Delta U + \Delta(PV) = \Delta U + P\Delta V \\ &= \Delta U + RT \\ &= 37.59 \text{ kJ mol}^{-1} + (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(373.15 \text{ K}) \\ &= 40.69 \text{ kJ mol}^{-1} \end{aligned}$$

1.11 Calculate $H^\circ(2\,000 \text{ K}) - H^\circ(0 \text{ K})$ for $\text{H}(\text{g})$.

SOLUTION

Equation 1.69 may be integrated to obtain

$$H^\circ(T_2) - H^\circ(T_1) = \int_{T_1}^{T_2} C_P^\circ \, dT$$

$$\begin{aligned} H^\circ(2\,000 \text{ K}) - H^\circ(0 \text{ K}) &= \int_0^{2\,000} \frac{5}{2} R \, dT = \frac{5}{2} R(2\,000) \\ &= 41.572 \text{ kJ mol}^{-1} \end{aligned}$$

Table A.2 yields $6.197 + 35.376 = 41.573 \text{ kJ mol}^{-1}$

(Note that for $\text{O}(\text{g})$ a slightly higher value is obtained because there is some absorption of heat by excitation to higher electronic levels.)

1.12 Considering H_2O to be a rigid nonlinear molecule, what value of C_p for the gas would be expected classically? If vibration is taken into account, what value is expected? Compare these values of C_p with the actual values at 298 and 3000 K in Table A.1.

SOLUTION

A rigid molecule has translational and rotational energy. The translational contribution to C_V is $\frac{3}{2} R = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$.

Since H_2O is a nonlinear molecule, it has three rotational degrees of freedom, and so the rotational contribution to C_V is $\frac{3}{2} R = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$.

Thus C_p for the rigid molecule is

$$C_p = C_V + R = 33.258 \text{ J K}^{-1} \text{ mol}^{-1}$$

Since H_2O is a nonlinear molecule, the number of vibrational degrees of freedom is $3N - 6 = 3$. Since each vibrational degree of freedom contributes R to the heat capacity, classical theory predicts

$$\begin{aligned} C_p &= 33.258 \text{ J K}^{-1} \text{ mol}^{-1} + 3R \\ &= 58.201 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The experimental value of C_p at 298 K is $33.577 \text{ J K}^{-1} \text{ mol}^{-1}$, which is only slightly higher than the value expected for a rigid molecule. The experimental value of C_p at 3000 K is $55.664 \text{ J K}^{-1} \text{ mol}^{-1}$, which is only slightly less than the classical expectation for a vibrating water molecule.

- ✓1.13 The equation for the molar heat capacity of n-butane is $C_P = 19.41 + 0.233 T$ where C_P is given in $\text{J K}^{-1} \text{mol}^{-1}$. Calculate the heat necessary to raise the temperature of 1 mole from 25 to 300 °C at constant pressure.

SOLUTION

$$\begin{aligned}
 q &= \int_{T_1}^{T_2} C_P dT = 19.41(T_2 - T_1) + \frac{1}{2}(0.233)(T_2^2 - T_1^2) \\
 &= 19.41(573.15 - 298.15) + \frac{1}{2}(0.233) \\
 &\quad (573.15^2 - 298.15^2) \\
 &= 33.31 \text{ kJ mol}^{-1}
 \end{aligned}$$

- ✓1.14 One mole of nitrogen at 25 °C and 1 atm is expanded reversibly and isothermally to a pressure of 0.132 bar. (a) What is the value of w ? What is the value of w if the temperature is 100 °C?

SOLUTION

$$\begin{aligned}
 \text{(a) } w &= -\int_{P_1}^{P_2} PdV = -RT \ln \frac{P_1}{P_2} \\
 &= -(8.314 \text{ J K}^{-1} \text{mol}^{-1})(298.15 \text{ K}) \ln \frac{1}{0.132} \\
 &= -5027 \text{ J mol}^{-1} \\
 \text{(b) } w &= (-5027 \text{ J mol}^{-1})(373.15 \text{ K}) / (298.15 \text{ K}) \\
 &= -6292 \text{ J mol}^{-1}
 \end{aligned}$$

- ✓1.15 Calculate the temperature increase and final pressure of helium if a mole is compressed adiabatically and reversibly from 44.8 L at 0 °C to 22.4 L.

SOLUTION

$$\gamma = C_P/C_V = \left(\frac{5}{2} R\right) / \left(\frac{3}{2} R\right) = \frac{5}{3}$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$T_2 = (273.15 \text{ K}) (44.8 \text{ L}/22.4 \text{ L})^{2/3}$$

$$= 433.6 \text{ K} \quad \text{or} \quad 160.4 \text{ }^\circ\text{C}$$

Thus the temperature increase is 160.4 °C.
The final temperature is given by

$$P = \frac{RT}{V} = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}) (433.6 \text{ K})}{22.4 \text{ L mol}^{-1}}$$

$$= 1.609 \text{ bar}$$

- ✓1.16 A mole of argon is allowed to expand adiabatically from a pressure of 10 bar and 298.15 K to 1 bar. What is the final temperature and how much work can be done?

SOLUTION

$$\gamma = C_P/C_V = \left(\frac{5}{2} R\right) / \left(\frac{3}{2} R\right) = \frac{5}{3}$$

$$(\gamma-1)/\gamma = 2/5$$

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma}$$

$$T_2 = (298.15 \text{ K}) (1/10)^{2/5} = 118.70 \text{ K}$$

$$w = \int_{T_1}^{T_2} C_V dT = \frac{3}{2} R (T_2 - T_1)$$

$$= \frac{3}{2} (8.314 \text{ K}^{-1} \text{ mol}^{-1}) (118.70 \text{ K} - 298.15 \text{ K})$$

$$= 2238 \text{ J mol}^{-1}$$

Thus the maximum work that can be done on the surroundings is 2238 J mol⁻¹.

1.17 A tank contains 20 liters of compressed nitrogen at 10 bar and 25 °C. Calculate the maximum work (in joules) which can be obtained when gas is allowed to expand to 1 bar pressure (a) isothermally and (b) adiabatically.

SOLUTION

(a) For the isothermal expansion of 1 mol

$$\begin{aligned} w_{\text{rev}} &= -RT \ln \frac{P_2}{P_1} \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln 10 \\ &= -5708 \text{ J mol}^{-1} \end{aligned}$$

There are

$$(10 \text{ bar})(20 \text{ L}) / (0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = 8.07 \text{ mol.}$$

Therefore the maximum work done on the surroundings is 46.1 kJ.

(b) For the adiabatic expansion we will assume that $\gamma = C_p/C_V$ has the value it has at room temperature. From Table A.2

$$\gamma = 29.125 / (29.125 - 8.314) = 1.399$$

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2} \right)^{(\gamma-1)/\gamma}$$

$$T_2 = (298.15 \text{ K})(1/10)^{0.285} = 154.7 \text{ K}$$

$$\begin{aligned} w &= \int_{T_1}^{T_2} C_V dT = C_V(T_2 - T_1) \\ &= (20.811 \text{ J K}^{-1} \text{ mol}^{-1})(154.7 - 298.15 \text{ K}) \\ &= -2.99 \text{ kJ mol}^{-1} \end{aligned}$$

For 8.07 moles the maximum work done on the surroundings is 24.1 kJ.

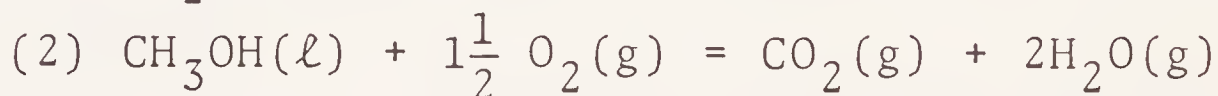
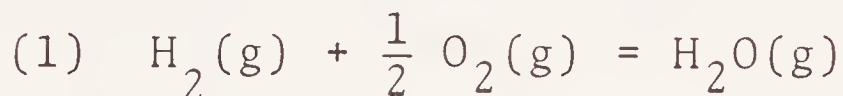
1.18 In an adiabatic calorimeter, oxidation of 0.4362 gram of naphthalene caused a temperature rise of

1.707 °C. The heat capacity of the calorimeter and water was 10,290 JK⁻¹. If corrections for oxidation of the wire and residual nitrogen are neglected, what is the enthalpy of combustion of naphthalene per mole?

SOLUTION

$$\begin{aligned}\Delta H &= \frac{(10,290 \text{ JK}^{-1})(1.707 \text{ K})(128.19 \text{ g mol}^{-1})}{(0.4362 \text{ g})(1000 \text{ cal kcal}^{-1})} \\ &= -5163 \text{ kJ mol}^{-1}\end{aligned}$$

1.19 The following reactions might be used to power rockets.



(a) Calculate the enthalpy changes at 25 °C for each of these reactions per kilogram of reactants

(b) Since the thrust is greater when the molar mass of the exhaust gas is lower, divide the heat per kilogram by the molar mass of the product (or the average molar mass in the case of reaction 2) and arrange the above reactions in order of effectiveness on the basis of thrust.

SOLUTION

$$\begin{aligned}(a) (1) \quad \Delta H &= -241.818 \text{ kJ mol}^{-1} \\ &= (-241.818 \text{ kJ mol}^{-1})(1000 \text{ g kg}^{-1})/(18 \text{ g mol}^{-1}) \\ &= -13.4 \text{ MJ kg}^{-1}\end{aligned}$$

$$\begin{aligned}(2) \quad \Delta H &= -393.509 + 2(-241.818) + 238.66 \\ &= -638.49 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}
 &= (-638.49 \text{ kJ mol}^{-1})(1000 \text{ g kg}^{-1}) / (80 \text{ g mol}^{-1}) \\
 &= -7.98 \text{ MJ kg}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 (3) \quad \Delta H &= 2(-271.1) = -542.2 \text{ kJ mol}^{-1} \\
 &= (-542.2 \text{ kJ mol}^{-1})(1000 \text{ g kg}^{-1}) / (40 \text{ g mol}^{-1}) \\
 &= -13.6 \text{ MJ kg}^{-1}
 \end{aligned}$$

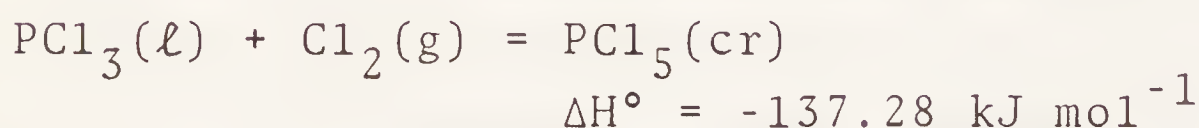
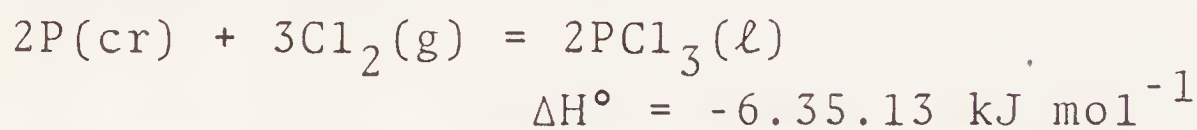
$$(b) \quad (1) \quad -13.4/18 = -0.744$$

$$(2) \quad \frac{-7.98}{\frac{1}{3}(44 + 2 \times 18)} = -0.299$$

$$(3) \quad -13.6/20 = -0.680$$

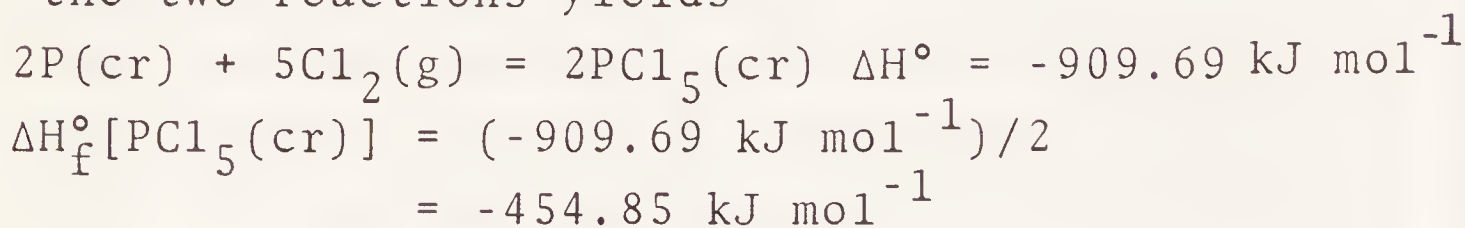
$$\therefore (1) > (3) > (2)$$

1.20 Calculate the enthalpy of formation of $\text{PCl}_5(\text{cr})$, given the heats of the following reactions at 25°C .



SOLUTION

Multiplying the second reaction by 2 and adding the two reactions yields



1.21 Calculate ΔH° for the dissociation $\text{O}_2(\text{g}) = 2\text{O}(\text{g})$ at 0, 298, and 3000 K. In Section 12.1 the enthalpy change for dissociation at 0 K will be found to be equal to the spectroscopic dissociation energy D_0 .

SOLUTION

$$\Delta H^\circ (0 \text{ K}) = 2(246.785) = 493.570 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ (298 \text{ K}) = 2(249.170) = 498.340 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ (3000 \text{ K}) = 2(256.722) = 513.444 \text{ kJ mol}^{-1}$$

The spectroscopic dissociation energy of O_2 is given as 5.115 eV in Table 13.4. This can be converted to kJ mol^{-1} by multiplying by $96.485 \text{ kJ V}^{-1} \text{ mol}^{-1}$ to obtain $493.521 \text{ kJ mol}^{-1}$.

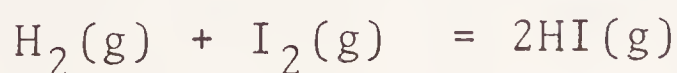
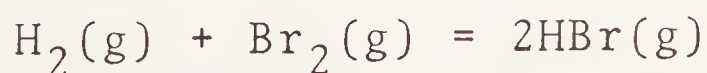
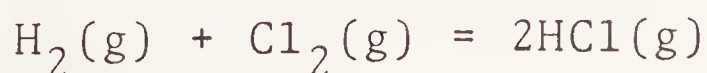
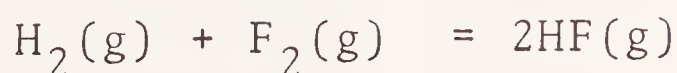
- 1.22 Compare the enthalpies of combustion of $\text{CH}_4(\text{g})$ to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ at 298 and 2000 K.

SOLUTION

$$\begin{aligned} \Delta H^\circ (298 \text{ K}) &= -393.522 + 2(-241.827) - (-74.873) \\ &= -802.303 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta H^\circ (2000 \text{ K}) &= -396.639 + 2(-251.668) - (-92.462) \\ &= -807.513 \text{ kJ mol}^{-1} \end{aligned}$$

- 1.23 Calculate ΔH_{298}° for

SOLUTION

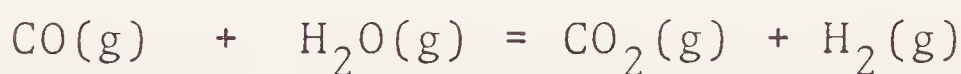
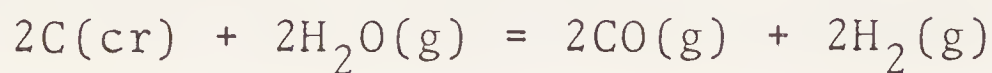
$$(a) \quad 2(-271.1) = -542.2 \text{ kJ mol}^{-1}$$

$$(b) \quad 2(-92.31) = -184.62 \text{ kJ mol}^{-1}$$

$$(c) \quad 2(-36.40) - -30.91 = -103.71 \text{ kJ mol}^{-1}$$

$$(d) \quad 2(26.48) - 62.44 = -9.48 \text{ kJ mol}^{-1}$$

1.24 Methane may be produced from coal in a process represented by the following steps, where coal is approximated by graphite:



The sum of these three reactions is



What is ΔH° at 500 K for each of these reactions?

Check that the sum of the ΔH° 's of the first three reactions is equal to ΔH° for the fourth reaction. From the standpoint of heat balance would it be better to develop a process to carry out the overall reactions in three separate reactors, or in a single reactor?

SOLUTION

$$\Delta H_{500}^\circ = 2(-110.02) - 2(-243.83) = 267.62 \text{ kJ mol}^{-1}$$

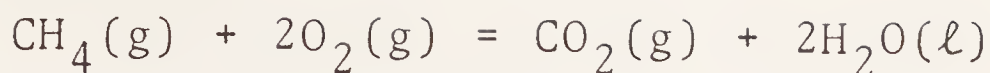
$$\Delta H_{500}^\circ = -393.68 - (-110.02) - (-243.83) = -39.83 \text{ kJ mol}^{-1}$$

$$\Delta H_{500}^\circ = -80.82 - 243.83 - (-110.02) = -214.63 \text{ kJ mol}^{-1}$$

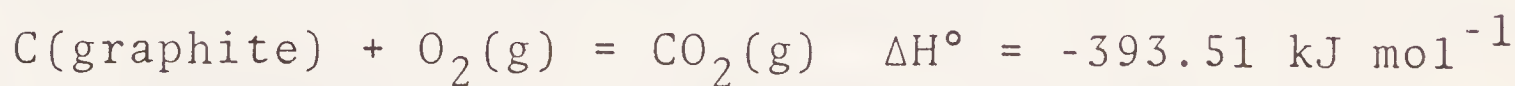
$$\Delta H_{500}^\circ = -80.82 - 393.68 - 2(-243.83) = 13.16 \text{ kJ mol}^{-1}$$

Since the first reaction is very endothermic, there is an advantage in carrying the subsequent reactions out in the same reactor so that they can provide heat.

1.25 Compare the enthalpy of combustion of $\text{CH}_4(\text{g})$ to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ at 298 K with the sum of the enthalpies of combustion of graphite and $2\text{H}_2(\text{g})$, from which $\text{CH}_4(\text{g})$ can in principle be produced.

SOLUTION

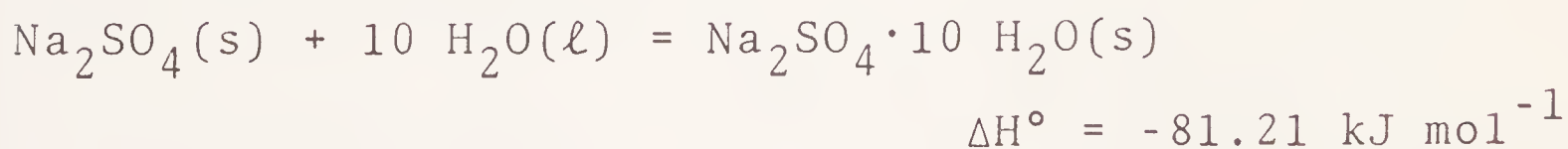
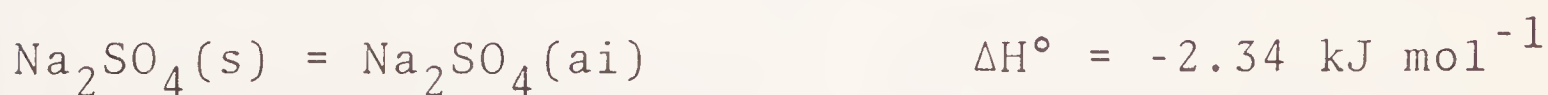
$$\begin{aligned}\Delta H^\circ(298 \text{ K}) &= -393.51 + 2(-285.83) - (-74.81) \\ &= -890.36 \text{ kJ mol}^{-1}\end{aligned}$$



The sum of the enthalpy changes for the last two reactions ($-965.17 \text{ kJ mol}^{-1}$) is more negative than the enthalpy change for the first reaction by the enthalpy of formation of $\text{CH}_4(\text{g})$.

1.26 Calculate the heat of hydration of $\text{Na}_2\text{SO}_4(\text{s})$

from the integral heats of solution of $\text{Na}_2\text{SO}_4(\text{s})$ and $\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}(\text{s})$ in infinite amounts of H_2O , which are $-2.34 \text{ kJ mol}^{-1}$ and $78.87 \text{ kJ mol}^{-1}$, respectively. Enthalpies of hydration cannot be measured directly because of the slowness of the phase transition.

SOLUTION

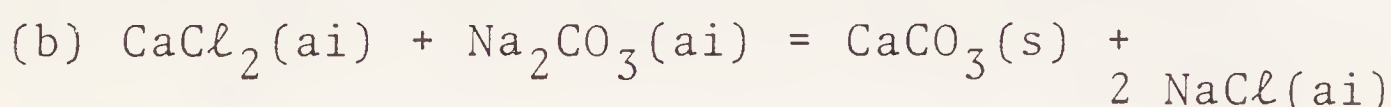
1.27 Calculate the integral heat of solution of one mole of $\text{HCl}(\text{g})$ in $200 \text{ H}_2\text{O}(\ell)$.



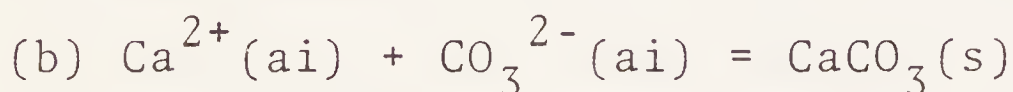
SOLUTION

$$\begin{aligned}\Delta H^\circ_{298} &= \Delta H^\circ_{f, \text{HCl in } 200 \text{ H}_2\text{O}} - \Delta H^\circ_{f, \text{HCl(g)}} \\ &= -166.272 - (-92.307) \\ &= -73.965 \text{ kJ mol}^{-1}\end{aligned}$$

1.28 Calculate the enthalpies of reaction at 25 °C for the following reactions in dilute aqueous solutions:

SOLUTION

(a) $\Delta H^\circ = 0$ because all of the reactants and products are completely ionized.



$$\begin{aligned}\Delta H^\circ &= -1206.92 - (-542.83) - (-677.14) \\ &= 13.05 \text{ kJ mol}^{-1}\end{aligned}$$

1.29 The heat capacities of a gas may be represented

by $C_p = a + bT + cT^2$

For N_2 , $a = 26.984$, $b = 5.910 \times 10^{-3}$, and $c = -3.377 \times 10^{-7}$, when C_p is expressed in $\text{J K}^{-1} \text{mol}^{-1}$. How much heat is required to heat a mole of N_2 from 300 K to 1000 K?

SOLUTION

$$\begin{aligned}q &= \int_{300}^{1000} (26.984 + 5.910 \times 10^{-3}T - 3.377 \times 10^{-7}T^2) dT \\ &= 26.984(1000 - 300) + \frac{1}{2}(5.910 \times 10^{-3})(1000^2 - 300^2) - \\ &\quad \frac{1}{3}(3.377 \times 10^{-7})(1000^3 - 300^3) \\ &= 21.468 \text{ kJ mol}^{-1}\end{aligned}$$

- 1.48 $40,874 \text{ J mol}^{-1}$
 1.49 (a) 13.075 , (b) $10.598 \text{ kJ mol}^{-1}$
 1.50 (a) $-74.5 \text{ L bar mol}^{-1}$ (b) 7448 J mol^{-1} (c) 0
 (d) 0
 1.51 (a) 567 K (b) 9.42 bar (c) 5527 J mol^{-1}
 1.52 (a) 0.495 , (b) 0.307 bar
 1.53 (a) 41.84 , (b) 25.56 kJ
 1.54 2.91 kWh 0.172 4.4 kg
 1.55
 $\text{C}(\text{cr}) + 2\text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$

$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g})$	$\uparrow 74.9$		
$\text{CO}_2(\text{g}) + 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$		$\downarrow -393.5$	
$\text{C}(\text{cr}) + 2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g})$			$\downarrow -571.7$
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$		$\downarrow -393.5$	$\downarrow -890.4$

- 1.56 (a) -253.42 , (b) $-249.70 \text{ kJ mol}^{-1}$
 1.57 $-41.51 \text{ kJ mol}^{-1}$
 1.58 $12.01 \text{ kJ mol}^{-1}$
 1.59 $-585 \pm 8 \text{ kJ mol}^{-1}$ and $-589 \pm 2 \text{ kJ mol}^{-1}$
 1.60 (a) -120.9 , (b) -50.2 , (c) -19.92 ,
 (d) $-45.2 \text{ kJ mol}^{-1}$
 1.61 $225.756 \text{ kJ mol}^{-1}$ is absorbed.
 1.62 -214.627 , -800.521 , $-1015.148 \text{ kJ mol}^{-1}$
 1.63 432.074 , 435.998 , $459.578 \text{ kJ mol}^{-1}$
 1.64 214.627 , -97.92 , $116.71 \text{ kJ mol}^{-1}$. Single
 reactor
 1.65 (a) -94.1 , (b) $-359.0 \text{ kJ mol}^{-1}$
 1.66 2432.6 J g^{-1}

CHAPTER 2. Second and Third Laws of Thermodynamics

2.1 Theoretically, how high could a gallon of gasoline lift an automobile weighing 2800 lb against the force of gravity, if it is assumed that the cylinder temperature is 2200 K and the exit temperature 1200 K? (Density of gasoline = 0.80 g cm⁻³; 1 lb = 453.6 g; 1 ft = 30.48 cm; 1 liter = 0.2642 gal. Heat of combustion of gasoline = 46.9 kJ g⁻¹.)

SOLUTION

$$\begin{aligned} q &= \frac{(46.9 \times 10^3 \text{ J g}^{-1})(1 \text{ gal.})(10^3 \text{ cm}^3 \text{ L}^{-1})(0.80 \text{ g cm}^{-3})}{0.2642 \text{ gal. L}^{-1}} \\ &= 14.2 \times 10^7 \text{ J} \\ w &= q \frac{T_2 - T_1}{T_2} = \frac{(14.2 \times 10^7 \text{ J})(2200 \text{ K} - 1200 \text{ K})}{(2200 \text{ K})} \\ &= 6.45 \times 10^7 \text{ J} \\ &= mgh = (2800 \text{ lb})(0.4536 \text{ kg lb}^{-1})(9.8 \text{ m s}^{-2}) \times \\ & \hspace{15em} (0.3048 \text{ m ft}^{-1})h \\ h &= 17,000 \text{ ft} \end{aligned}$$

2.2 (a) What is the maximum work that can be obtained from 1000 J of heat supplied to a water boiler at 100 °C if the condenser is at 20 °C?
(b) If the boiler temperature is raised to 150 °C by the use of superheated steam under pressure, how much more work can be obtained?

SOLUTION

$$(a) \quad w = q \frac{T_2 - T_1}{T_2} = (1000 \text{ J}) \frac{80 \text{ K}}{373.1 \text{ K}} = 214 \text{ J}$$

$$(b) w = (1000 \text{ J}) \frac{130 \text{ K}}{423.1 \text{ K}} = 307 \text{ J} \quad \text{or } 93 \text{ J more than (a)}$$

2.3 What is the entropy change for the freezing of one mole of water at 0 °C? The heat of fusion is 333.5 J g⁻¹.

SOLUTION

$$\begin{aligned} \Delta S &= \frac{\Delta H}{T} = \frac{-(333.5 \text{ J g}^{-1})(18.015 \text{ g mol}^{-1})}{273.15 \text{ K}} \\ &= -22.00 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

2.4 Calculate the increase in entropy of a mole of silver that is heated at constant pressure from 0 to 30 °C if the value of C_p in this temperature range is considered to be constant at 25.48 J K⁻¹ mol⁻¹.

SOLUTION

$$\begin{aligned} \Delta S &= C_p \ln \frac{T_2}{T_1} = (25.48 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{303}{273} \\ &= 2.657 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

2.5 Calculate the change in entropy of a mole of aluminum which is heated from 600 °C to 700 °C. The melting point of aluminum is 660 °C, the heat of fusion is 393 J g⁻¹, and the heat capacities of the solid and liquid may be taken as 31.8 and 34.3 J K⁻¹ mol⁻¹, respectively.

SOLUTION

$$\Delta S = \int_{T_1}^{T_f} \frac{C_{P,s}}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_2} \frac{C_{P,l}}{T} dT$$