The Properties of Gases

PROBLEMS AND SOLUTIONS

16–1. In an issue of the journal *Science* a few years ago, a research group discussed experiments in which they determined the structure of cesium iodide crystals at a pressure of 302 gigapascals (GPa). How many atmospheres and bars is this pressure?

2.98×10^6 atm, 3.02×10^6 bar

16–2. In meteorology, pressures are expressed in units of millibars (mbar). Convert 985 mbar to torr and to atmospheres.

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739 torr, 0.972 atm

16–3. Calculate the value of the pressure (in atm) exerted by a 33.9-foot column of water. Take the density of water to be $1.00\ \text{g}\cdot\text{mL}^{-1}$.

We first convert the height of the column to metric units: 33.9 ft = 10.33 m. Now

$$P = \rho g h = (1.00\ \text{kg}\cdot\text{dm}^{-3})(98.067\ \text{dm}\cdot\text{s}^{-2})(103.3\ \text{dm})$$
$$= 1.013 \times 10^4\ \text{kg}\cdot\text{dm}^{-1}\cdot\text{s}^{-2}$$
$$= 1.013 \times 10^5\ \text{Pa} = 1.00\ \text{atm}$$

16–4. At which temperature are the Celsius and Farenheit temperature scales equal?

$-40°$

16–5. A travel guide says that to convert Celsius temperatures to Farenheit temperatures, double the Celsius temperature and add 30. Comment on this recipe.

This will provide a rough estimate of the temperature, decreasing in accuracy as temperature increases. (Of course, it is not valid for Celsius temperatures below zero degrees.) At room temperatures, it is accurate enough for ordinary purposes.

Actual T (°C)	Actual T (°F)	Travel T (°F)
0	32	30
10	50	50
20	68	70
30	86	90
40	104	110

16–6. Research in surface science is carried out using ultra-high vacuum chambers that can sustain pressures as low as 10^{-12} torr. How many molecules are there in a 1.00-cm^3 volume inside such an apparatus at 298 K? What is the corresponding molar volume $\overline{V}$ at this pressure and temperature?

We will assume ideal gas behavior, so

$$\frac{PV}{RT} = n \tag{16.1a}$$

$$\frac{(10^{-12}\text{ torr})(1.00\text{ cm}^3)}{(82.058\text{ cm}^3\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(760\text{ torr}\cdot\text{atm}^{-1})(298\text{ K})} = n$$

$$5.38\times 10^{-20}\text{ mol} = n$$

so there are 3.24×10^4 molecules in the apparatus. The molar volume is

$$\overline{V} = \frac{V}{n} = \frac{1.00\text{ cm}^3}{5.38\times 10^{-20}\text{ mol}} = 1.86\times 10^{19}\text{ cm}^3\cdot\text{mol}^{-1}$$

16–7. Use the following data for an unknown gas at 300 K to determine the molecular mass of the gas.

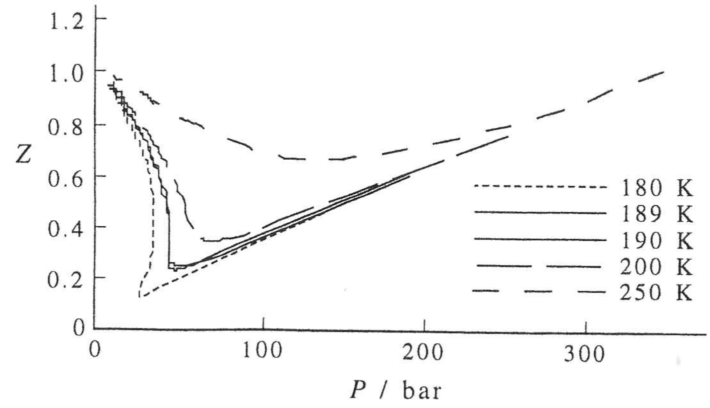
P/bar	0.1000	0.5000	1.000	1.01325	2.000
ρ/g·L^{-1}	0.1771	0.8909	1.796	1.820	3.652

The line of best fit of a plot of P/ρ versus ρ will have an intercept of RT/M. Plotting, we find that the intercept of this plot is 0.56558 bar·g^{-1}·dm^3, and so $M = 44.10$ g·mol^{-1}.

16–8. Recall from general chemistry that Dalton's law of partial pressures says that each gas in a mixture of ideal gases acts as if the other gases were not present. Use this fact to show that the partial pressure exerted by each gas is given by

$$P_j = \left(\frac{n_j}{\sum n_j}\right) P_{\text{total}} = y_j P_{\text{total}}$$

where P_j is the partial pressure of the jth gas and y_j is its mole fraction.



16–15. Use both the van der Waals and the Redlich-Kwong equations to calculate the molar volume of CO at 200 K and 1000 bar. Compare your result to the result you would get using the ideal-gas equation. The experimental value is $0.04009\ \text{L}\cdot\text{mol}^{-1}$.

We can use the Newton-Raphson method (MathChapter G) to solve these cubic equations of state. We can express $f(\overline{V})$ for the van der Waals equation as (Example 16–2)

$$f(\overline{V}) = \overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P}$$

and $f'(\overline{V})$ as

$$f'(\overline{V}) = 3\overline{V}^2 - 2\left(b + \frac{RT}{P}\right)\overline{V} + \frac{a}{P}$$

For CO, $a = 1.4734\ \text{dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}$ and $b = 0.039523\ \text{dm}^3\cdot\text{mol}^{-1}$ (Table 16.3). Then, using the Newton-Raphson method, we find that the van der Waals equation gives a result of $\overline{V} = 0.04998\ \text{dm}^3\cdot\text{mol}^{-1}$. Likewise, we can express $f(\overline{V})$ for the Redlich-Kwong equation as (Equation 16.9)

$$f(\overline{V}) = \overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\overline{V} - \frac{AB}{T^{1/2}P}$$

and $f'(\overline{V})$ as

$$f'(\overline{V}) = 3\overline{V}^2 - \frac{2RT}{P}\overline{V} - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)$$

For CO, $A = 17.208\ \text{dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}\cdot\text{K}^{1/2}$ and $B = 0.027394\ \text{dm}^3\cdot\text{mol}^{-1}$ (Table 16.4). Applying the Newton-Raphson method, we find that the Redlich-Kwong equation gives a result of $\overline{V} = 0.03866\ \text{dm}^3\cdot\text{mol}^{-1}$. Finally, the ideal gas equation gives (Equation 16.1)

$$\overline{V} = \frac{RT}{P} = \frac{(0.083145\ \text{dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(200\ \text{K})}{1000\ \text{bar}} = 0.01663\ \text{dm}^3\cdot\text{mol}^{-1}$$

The experimental value of $0.04009\ \text{dm}^3\cdot\text{mol}^{-1}$ is closest to the result given by the Redlich-Kwong equation (the two values differ by about 3%).

16–16. Compare the pressures given by (a) the ideal-gas equation, (b) the van der Waals equation, (c) the Redlich-Kwong equation, and (d) the Peng-Robinson equation for propane at 400 K and $\rho = 10.62\ \text{mol}\cdot\text{dm}^{-3}$. The experimental value is 400 bar. Take $\alpha = 9.6938\ \text{L}^2\cdot\text{mol}^{-2}$ and $\beta = 0.05632\ \text{L}\cdot\text{mol}^{-1}$ for the Peng-Robinson equation.

The molar volume corresponding to a density of 10.62 $mol\cdot dm^{-3}$ is 0.09416 $dm^3\cdot mol^{-1}$.

a. The ideal gas equation gives a pressure of (Equation 16.1)

$$P = \frac{RT}{\overline{V}} = \frac{(0.083145\ dm^3\cdot bar\cdot mol^{-1}\cdot K^{-1})(400\ K)}{0.09416\ dm^3\cdot mol^{-1}} = 353.2\ bar$$

b. The van der Waals equation gives a pressure of (Equation 16.5)

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

For propane, $a = 9.3919\ dm^6\cdot bar\cdot mol^{-2}$ and $b = 0.090494\ dm^3\cdot mol^{-1}$ (Table 16.3). Then

$$P = \frac{(0.083145\ dm^3\cdot bar\cdot mol^{-1}\cdot K^{-1})(400\ K)}{0.09416\ dm^3\cdot mol^{-1} - 0.090494\ dm^3\cdot mol^{-1}} - \frac{9.3919\ dm^6\cdot bar\cdot mol^{-2}}{(0.09416\ dm^3\cdot mol^{-1})^2}$$
$$= 8008\ bar$$

c. The Redlich-Kwong equation gives a pressure of (Equation 16.7)

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)}$$

For propane, $A = 183.02\ dm^6\cdot bar\cdot mol^{-2}\cdot K^{1/2}$ and $B = 0.062723\ dm^3\cdot mol^{-1}$ (Table 16.4). Then

$$P = \frac{(0.083145\ dm^3\cdot bar\cdot mol^{-1}\cdot {}^{-1})(400\ K)}{0.09416\ dm^3\cdot mol^{-1} - 0.062723\ dm^3\cdot mol^{-1}}$$
$$- \frac{183.02\ dm^6\cdot bar\cdot mol^{-2}\cdot K^{1/2}}{(400\ K)^{1/2}(0.09416\ dm^3\cdot mol^{-1})(0.09416\ dm^3\cdot mol^{-1} + 0.062723\ dm^3\cdot mol^{-1})}$$
$$= 438.4\ bar$$

d. The Peng-Robinson equation gives a pressure of (Equation 16.8)

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)}$$

For propane, $\alpha = 9.6938\ dm^6\cdot bar\cdot mol^{-2}$ and $\beta = 0.05632\ dm^3\cdot mol^{-1}$. Then

$$P = \frac{(0.083145\ dm^3\cdot bar\cdot mol^{-1}\cdot {}^{-1})(400\ K)}{0.09416\ dm^3\cdot mol^{-1} - 0.05632\ dm^3\cdot mol^{-1}}$$
$$- \frac{9.6938\ dm^6\cdot bar\cdot mol^{-2}}{(0.09416)(0.09416 + 0.05632)\ dm^6\cdot mol^{-2} + (0.05632)(0.09416 - 0.05632)\ dm^6\cdot mol^{-2}}$$
$$= 284.2\ bar$$

The Redlich-Kwong equation of state gives a pressure closest to the experimentally observed pressure (the two values differ by about 10%).

16–17. Use the van der Waals equation and the Redlich-Kwong equation to calculate the value of the pressure of one mole of ethane at 400.0 K confined to a volume of 83.26 cm^3. The experimental value is 400 bar.

Here, the molar volume of ethane is 0.08326 $dm^3\cdot mol^{-1}$.

CHAPTER 19

The First Law of Thermodynamics

PROBLEMS AND SOLUTIONS

19–1. Suppose that a 10-kg mass of iron at 20°C is dropped from a height of 100 meters. What is the kinetic energy of the mass just before it hits the ground? What is its speed? What would be the final temperature of the mass if all its kinetic energy at impact is transformed into internal energy? Take the molar heat capacity of iron to be $\overline{C}_P = 25.1\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and the gravitational acceleration constant to be $9.80\ \text{m}\cdot\text{s}^{-2}$.

Just before the mass hits the ground, all of the potential energy that the mass originally had will be converted into kinetic energy. So

$$\text{PE} = mgh = (10\ \text{kg})(9.80\ \text{m}\cdot\text{s}^{-2})(100\ \text{m}) = 9.8\ \text{kJ} = \text{KE}$$

Since kinetic energy can be expressed as $mv^2/2$, the speed of the mass just before hitting the ground is

$$v_f = \left(\frac{2\text{KE}}{m}\right)^{1/2} = \left[\frac{2(9.8\ \text{kJ})}{10\ \text{kg}}\right]^{1/2} = 44\ \text{m}\cdot\text{s}^{-1}$$

For a solid, the difference between $\overline{C}_V$ and $\overline{C}_P$ is small, so we can write $\Delta U = n\overline{C}_P\Delta T$ (Equation 19.39). Then

$$\Delta T = \frac{9.8\ \text{kJ}}{\left(\dfrac{1\times 10^4\ \text{g}}{55.85\ \text{g}\cdot\text{mol}^{-1}}\right)(25.1\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})} = 2.2\ \text{K}$$

The final temperature of the iron mass is then 22.2°C.

19–2. Consider an ideal gas that occupies 2.50 dm^3 at a pressure of 3.00 bar. If the gas is compressed isothermally at a constant external pressure, P_{ext}, so that the final volume is 0.500 dm^3, calculate the smallest value P_{ext} can have. Calculate the work involved using this value of P_{ext}.

Since the gas is ideal, we can write

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(3.00\ \text{bar})(2.50\ \text{dm}^3)}{0.500\ \text{dm}^3} = 15.0\ \text{bar}$$

The smallest possible value of P_{ext} is P_2. The work done in this case is (Equation 19.1)

$$w = -P_{\text{ext}}\Delta V = (-15.0\ \text{bar})(-2.0\ \text{dm}^3)\left(\frac{8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}{0.083145\ \text{bar}\cdot\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}\right) = 3000\ \text{J}$$

19–3. A one-mole sample of $CO_2(g)$ occupies 2.00 dm^3 at a temperature of 300 K. If the gas is compressed isothermally at a constant external pressure, P_{ext}, so that the final volume is 0.750 dm^3, calculate the smallest value P_{ext} can have, assuming that $CO_2(g)$ satisfies the van der Waals equation of state under these conditions. Calculate the work involved using this value of P_{ext}.

The smallest value P_{ext} can have is P_2, where P_2 is the final pressure of the gas. We can use the van der Waals equation (Equation 16.5) and the constants given in Table 16.3 to find P_2:

$$
\begin{aligned}
P_2 &= \frac{RT_2}{\overline{V}_2 - b} - \frac{a}{\overline{V}_2^2} \\
&= \frac{(0.083145\ \text{dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300\ \text{K})}{0.750\ \text{dm}^3\cdot\text{mol}^{-1} - 0.042816\ \text{dm}^3\cdot\text{mol}^{-1}} - \frac{3.6551\ \text{dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}}{(0.750\ \text{dm}^3\cdot\text{mol}^{-1})^2} \\
&= 28.8\ \text{bar}
\end{aligned}
$$

The work involved is (Equation 19.1)

$$w = -P\Delta V = -(28.8 \times 10^5\ \text{Pa})(-1.25 \times 10^{-3}\ \text{m}^3) = 3.60\ \text{kJ}$$

19–4. Calculate the work involved when one mole of an ideal gas is compressed reversibly from 1.00 bar to 5.00 bar at a constant temperature of 300 K.

Using the ideal gas equation, we find that

$$V_1 = \frac{nRT}{P_1} \qquad \text{and} \qquad V_2 = \frac{nRT}{P_2}$$

We can therefore write $V_2/V_1 = P_1/P_2$. Now we substitute into Equation 19.2 to find

$$
\begin{aligned}
w &= -\int P_{ext} dV = -\int \frac{nRT}{V} dV \\
&= -nRT \ln\left(\frac{V_2}{V_1}\right) = -nRT \ln\left(\frac{P_1}{P_2}\right) \\
&= (-1\ \text{mol})(8.315\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300\ \text{K}) \ln 0.2 = 4.01\ \text{kJ}
\end{aligned}
$$

19–5. Calculate the work involved when one mole of an ideal gas is expanded reversibly from 20.0 dm^3 to 40.0 dm^3 at a constant temperature of 300 K.

We can integrate Equation 19.2 to find the work involved:

$$
\begin{aligned}
w &= -nRT \ln\left(\frac{V_2}{V_1}\right) \\
&= (-1\ \text{mol})(8.315\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300\ \text{K}) \ln 2 = -1.73\ \text{kJ}
\end{aligned}
$$

19–6. Calculate the minimum amount of work required to compress 5.00 moles of an ideal gas isothermally at 300 K from a volume of 100 dm^3 to 40.0 dm^3.

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and, finally,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P}$$

19–18. Show that

$$P_1 V_1^{(\overline{C}_V + R)/\overline{C}_V} = P_2 V_2^{(\overline{C}_V + R)/\overline{C}_V}$$

for an adiabatic expansion of an ideal gas. Show that this formula reduces to Equation 19.23 for a monatomic gas.

For an ideal gas,

$$\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$$

We can substitute this expression into the equation from Problem 19–15 to write

$$\frac{P_1 V_1}{P_2 V_2} = \left(\frac{V_1}{V_2}\right)^{R/\overline{C}_V}$$

Taking the reciprocal gives

$$\frac{P_1 V_1}{P_2 V_2} = \left(\frac{V_2}{V_1}\right)^{R/\overline{C}_V}$$

and rearranging yields

$$P_1 V_1^{\left(1 + R/\overline{C}_V\right)} = P_2 V_2^{\left(1 + R\overline{C}_V\right)}$$

For a monatomic ideal gas, $\overline{C}_V = \frac{3}{2}R$, so

$$P_1 V_1^{5/3} = P_2 V_2^{5/3} \qquad (19.23)$$

19–19. Calculate the work involved when one mole of a monatomic ideal gas at 298 K expands reversibly and adiabatically from a pressure of 10.00 bar to a pressure of 5.00 bar.

Because this process is adiabatic, $\delta q = 0$. This means that

$$\delta w = dU = n\overline{C}_V dT$$

where $\overline{C}_V$ is temperature-independent (since the gas is ideal). We can use the equation from Problem 19–17 to write

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P}$$

For an ideal gas, $\overline{C}_P = 5R/2$, so

$$T_2 = (298\text{ K}) \left(\frac{5.00\text{ bar}}{10.00\text{ bar}}\right)^{2/5} = 226\text{ K}$$

19–24. Liquid sodium is being considered as an engine coolant. How many grams of sodium are needed to absorb 1.0 MJ of heat if the temperature of the sodium is not to increase by more than 10°C. Take $\overline{C}_P = 30.8\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Na(l) and $75.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for H_2O(l).

We must have a coolant which can absorb 1.0×10^6 J without changing its temperature by more than 10 K. The smallest amount of sodium required will allow the temperature to change by exactly 10 K. We can consider this a constant-pressure process, because liquids are relatively incompressible. Then, substituting $\Delta T = 10$ K into Equation 19.40, we find

$$\Delta\overline{H} = \overline{C}_P \Delta T = 308\ \text{J}\cdot\text{mol}^{-1}$$

We require one mole of sodium to absorb 308 J of heat. Therefore, to absorb 1.0 MJ of heat, we require

$$(1.0 \times 10^6\ \text{J}) \left(\frac{1\ \text{mol}}{308\ \text{J}}\right) \left(\frac{22.99\ \text{g}}{1\ \text{mol}}\right) = 74.6\ \text{kg}$$

74.6 kg of liquid sodium is needed.

19–25. A 25.0-g sample of copper at 363 K is placed in 100.0 g of water at 293 K. The copper and water quickly come to the same temperature by the process of heat transfer from copper to water. Calculate the final temperature of the water. The molar heat capacity of copper is $24.5\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and that of water is $75.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

The heat lost by the copper is gained by the water. Since $\Delta H = n\overline{C}_P \Delta T$ (Equation 19.40), we can let x be the final temperature of the system and write the heat lost by the copper as

$$\left(\frac{25.0\ \text{g}}{63.546\ \text{g}\cdot\text{mol}^{-1}}\right) (24.5\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(363\ \text{K} - x)$$

and the heat gained by the water as

$$\left(\frac{100.0\ \text{g}}{18.0152\ \text{g}\cdot\text{mol}^{-1}}\right) (75.3\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(x - 293\ \text{K})$$

Equating these two expressions gives

$$3495\ \text{J} - (9.628\ \text{J}\cdot\text{K}^{-1})x = (418.0\ \text{J}\cdot\text{K}^{-1})x - 1.224 \times 10^5\ \text{J}$$

$$1.259 \times 10^5\ \text{K} = 427.6x$$

$$295\ \text{K} = x$$

The final temperature of the water is 295 K.

19–26. A 10.0-kg sample of liquid water is used to cool an engine. Calculate the heat removed (in joules) from the engine when the temperature of the water is raised from 293 K to 373 K. Take $\overline{C}_P = 75.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for H_2O(l).

We can use Equation 19.40, where $\Delta T = 373\ \text{K} - 293\ \text{K} = 80$ K. This gives

$$\Delta H = n\overline{C}_P \Delta T = \left(\frac{10.0 \times 10^3\ \text{g}}{18.0152\ \text{g}\cdot\text{mol}^{-1}}\right) (75.2\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(80\ \text{K}) = 3340\ \text{kJ}$$

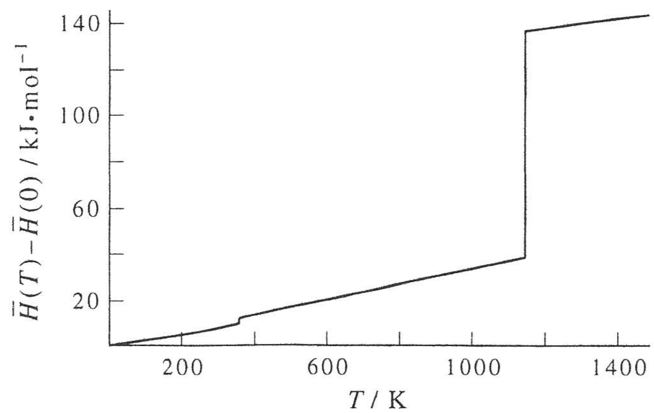
3340 kJ of heat is removed by the water.

19–34. Given the following data for sodium, plot $\overline{H}(T) - \overline{H}(0)$ against T for sodium: melting point, 361 K; boiling point, 1156 K; $\Delta_{\text{fus}} H^\circ = 2.60\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_{\text{vap}} H^\circ = 97.4\ \text{kJ}\cdot\text{mol}^{-1}$; $\overline{C}_P(\text{s}) = 28.2\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $\overline{C}_P(\text{l}) = 32.7\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $\overline{C}_P(\text{g}) = 20.8\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

We can use an extended form of Equation 19.46:

$$\overline{H}(T) - \overline{H}(0) = \int_0^{T_{\text{fus}}} \overline{C}_P(\text{s})dT + \Delta_{\text{fus}}\overline{H} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \overline{C}_P(\text{l})dT + \Delta_{\text{vap}}\overline{H} + \int_{T_{\text{vap}}}^{T} \overline{C}_P(\text{g})dT$$

Notice the very large jump between the liquid and gaseous phases.



19–35. The $\Delta_r H^\circ$ values for the following equations are

$$2\,\text{Fe(s)} + \tfrac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} \qquad \Delta_r H^\circ = -206\ \text{kJ}\cdot\text{mol}^{-1}$$

$$3\,\text{Fe(s)} + 2\,\text{O}_2\text{(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} \qquad \Delta_r H^\circ = -136\ \text{kJ}\cdot\text{mol}^{-1}$$

Use these data to calculate the value of $\Delta_r H$ for the reaction described by

$$4\,\text{Fe}_2\text{O}_3\text{(s)} + \text{Fe(s)} \longrightarrow 3\,\text{Fe}_3\text{O}_4\text{(s)}$$

Set up the problem so that the summation of two reactions will give the desired reaction:

$$\begin{array}{lr} 4[\text{Fe}_2\text{O}_3\text{(s)} \rightarrow 2\,\text{Fe(s)} + \tfrac{3}{2}\text{O}_2\text{(g)}] & \Delta_r H = 4(206)\ \text{kJ} \\ +\,3[3\,\text{Fe(s)} + 2\,\text{O}_2\text{(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)}] & \Delta_r H = 3(-136)\ \text{kJ} \\ \hline 4\,\text{Fe}_2\text{O}_3\text{(s)} + \text{Fe(s)} \longrightarrow 3\,\text{Fe}_3\text{O}_4\text{(s)} & \Delta_r H = 416\ \text{kJ} \end{array}$$

19–36. Given the following data,

$$\tfrac{1}{2}\text{H}_2\text{(g)} + \tfrac{1}{2}\text{F}_2\text{(g)} \rightarrow \text{HF(g)} \qquad \Delta_r H^\circ = -273.3\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)} \qquad \Delta_r H^\circ = -285.8\ \text{kJ}\cdot\text{mol}^{-1}$$

calculate the value of $\Delta_r H$ for the reaction described by

$$2\,\text{F}_2\text{(g)} + 2\,\text{H}_2\text{O(l)} \longrightarrow 4\,\text{HF(g)} + \text{O}_2\text{(g)}$$

Set up the problem so that the summation of two reactions will give the desired reaction:

$$4[\tfrac{1}{2}H_2(g) + \tfrac{1}{2}F_2(g) \rightarrow HF(g)] \qquad \Delta_r H = 4(-273.3)\text{ kJ}$$
$$+ \qquad 2[H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)] \qquad \Delta_r H = 2(285.8)\text{ kJ}$$
$$2\,F_2(g) + 2\,H_2O(l) \longrightarrow 4\,HF(g) + O_2(g) \qquad \Delta_r H = -521.6\text{ kJ}$$

19–37. The standard molar heats of combustion of the isomers *m*-xylene and *p*-xylene are -4553.9 kJ·mol^{-1} and -4556.8 kJ·mol^{-1}, respectively. Use these data, together with Hess's Law, to calculate the value of $\Delta_r H°$ for the reaction described by

$$m\text{-xylene} \longrightarrow p\text{-xylene}$$

Because *m*-xylene and *p*-xylene are isomers, their combustion equations are stoichiometrically equivalent. We can therefore write

$$m\text{-xylene} \rightarrow \text{combustion products} \qquad \Delta_r H = -4553.9\text{ kJ}$$
$$+\text{combustion products} \rightarrow p\text{-xylene} \qquad \Delta_r H = +4556.8\text{ kJ}$$
$$m\text{-xylene} \longrightarrow p\text{-xylene} \qquad \Delta_r H = +2.9\text{ kJ}$$

19–38. Given that $\Delta_r H° = -2826.7$ kJ for the combustion of 1.00 mol of fructose at 298.15 K,

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l)$$

and the $\Delta_f H°$ data in Table 19.2, calculate the value of $\Delta_f H°$ for fructose at 298.15 K.

We are given $\Delta_r H°$ for the combustion of fructose in the statement of the problem. We use the values given in Table 19.2 for $CO_2(g)$, $H_2O(l)$, and $O_2(g)$:

$$\Delta_f H°[CO_2(g)] = -393.509\text{ kJ·mol}^{-1} \qquad \Delta_f H°[H_2O(l)] = -285.83\text{ kJ·mol}^{-1}$$
$$\Delta_f H°[O_2(g)] = 0$$

Now, by Hess's law, we write

$$\Delta_r H° = \sum \Delta_f H°[\text{products}] - \sum \Delta_f H°[\text{reactants}]$$
$$-2826.7\text{ kJ·mol}^{-1} = 6(-393.509\text{ kJ·mol}^{-1}) + 6(-285.83\text{ kJ·mol}^{-1}) - \Delta_r H°[\text{fructose}]$$
$$\Delta_r H°[\text{fructose}] = 1249.3\text{ kJ·mol}^{-1}$$

19–39. Use the $\Delta_f H°$ data in Table 19.2 to calculate the value of $\Delta_c H°$ for the combustion reactions described by the equations:

a. $CH_3OH(l) + \tfrac{3}{2}\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$

b. $N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O(l)$

Compare the heat of combustion per gram of the fuels $CH_3OH(l)$ and $N_2H_4(l)$.

We will need the following values from Table 19.2:

$$\Delta_f H^\circ[CO_2(g)] = -393.509\ kJ\cdot mol^{-1} \qquad \Delta_f H^\circ[H_2O(l)] = -285.83\ kJ\cdot mol^{-1}$$
$$\Delta_f H^\circ[N_2H_4(l)] = +50.6\ kJ\cdot mol^{-1} \qquad \Delta_f H^\circ[CH_3OH(l)] = -239.1\ kJ\cdot mol^{-1}$$
$$\Delta_f H^\circ[N_2(g)] = 0$$

a. Using Hess's law,

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ[\text{products}] - \sum \Delta_f H^\circ[\text{reactants}]\\ &= 2(-285.83\ kJ) + (-393.5\ kJ) - (-239.1\ kJ)\\ &= \left(\frac{-726.1\ kJ}{\text{mol methanol}}\right)\left(\frac{1\ mol}{32.042\ g}\right) = -22.7\ kJ\cdot g^{-1}\end{aligned}$$

b. Again, by Hess's law,

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ[\text{products}] - \sum \Delta_f H^\circ[\text{reactants}]\\ &= 2(-285.83\ kJ) - (+50.6\ kJ)\\ &= \left(\frac{-622.3\ kJ}{\text{mol } N_2H_4}\right)\left(\frac{1\ mol}{32.046\ g}\right) = -19.4\ kJ\cdot g^{-1}\end{aligned}$$

More energy per gram is produced by combusting methanol.

19–40. Using Table 19.2, calculate the heat required to vaporize 1.00 mol of $CCl_4(l)$ at 298 K.

$$CCl_4(l) \longrightarrow CCl_4(g)$$

We can subtract $\Delta_f H^\circ[CCl_4(l)]$ from $\Delta_f H^\circ[CCl_4(g)]$ to find the heat required to vaporize CCl_4:

$$\Delta_{vap} H^\circ = -102.9\ kJ + 135.44\ kJ = 32.5\ kJ$$

19–41. Using the $\Delta_f H^\circ$ data in Table 19.2, calculate the values of $\Delta_r H^\circ$ for the following:

a. $C_2H_4(g) + H_2O(l) \longrightarrow C_2H_5OH(l)$

b. $CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_4(l) + 4\,HCl(g)$

In each case, state whether the reaction is endothermic or exothermic.

---

a. Using Hess's law,

$$\Delta_r H^\circ = -277.69\ kJ - (-285.83\ kJ + 52.28\ kJ) = -44.14\ kJ$$

This reaction is exothermic.

b. Again, by Hess's law,

$$\Delta_r H^\circ = 4(-92.31\ kJ) - 135.44\ kJ - (-74.81\ kJ) = -429.87\ kJ$$

This reaction is also exothermic.

19–42. Use the following data to calculate the value of $\Delta_{vap} H^\circ$ of water at 298 K and compare your answer to the one you obtain from Table 19.2: $\Delta_{vap} H^\circ$ at 373 K $= 40.7\ kJ\cdot mol^{-1}$; $\overline{C}_P(l) = 75.2\ J\cdot mol^{-1}\cdot K^{-1}$; $\overline{C}_P(g) = 33.6\ J\cdot mol^{-1}\cdot K^{-1}$.

We can solve this polynomial using Simpson's rule or a numerical software package. Working in *Mathematica*, we find that the final temperature will be 4040 K.

19–47. Explain why the adiabatic flame temperature defined in the previous problem is also called the maximum flame temperature.

The adiabatic flame temperature is the temperature of the system if all the energy released as heat stays within the system. Since we are considering an isolated system, the adiabatic flame temperature is also the maximum temperature which the system can achieve.

19–48. How much energy as heat is required to raise the temperature of 2.00 moles of $O_2(g)$ from 298 K to 1273 K at 1.00 bar? Take

$$\overline{C}_P[O_2(g)]/R = 3.094 + (1.561 \times 10^{-3}\ \text{K}^{-1})T - (4.65 \times 10^{-7}\ \text{K}^{-2})T^2$$

We can use Equation 19.44:

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} n\overline{C}_P dT \\ &= (2.00\ \text{mol})R\int_{298}^{1273}\left[3.094 + (1.561 \times 10^{-3}\ \text{K}^{-1})T - (4.65 \times 10^{-7}\ \text{K}^{-2})T^2\right]dT \\ &= 64.795\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

19–49. When one mole of an ideal gas is compressed adiabatically to one-half of its original volume, the temperature of the gas increases from 273 K to 433 K. Assuming that $\overline{C}_V$ is independent of temperature, calculate the value of $\overline{C}_V$ for this gas.

Equation 19.20 gives an expression for the reversible adiabatic expansion of an ideal gas:

$$\overline{C}_V dT = -\frac{RT}{V}dV$$

Integrating both sides and substituting the temperatures given, we find that

$$\begin{aligned}\int \frac{\overline{C}_V}{T}dT &= -\int \frac{R}{V}dV \\ \overline{C}_V \ln\frac{T_2}{T_1} &= -R\ln\frac{V_2}{V_1} \\ \overline{C}_V \ln\frac{433}{273} &= -R\ln 2 \\ \frac{\overline{C}_V}{R} &= 1.50\end{aligned}$$

19–50. Use the van der Waals equation to calculate the minimum work required to expand one mole of $CO_2(g)$ isothermally from a volume of 0.100 dm^3 to a volume of 100 dm^3 at 273 K. Compare your result with that which you calculate assuming ideal behavior.

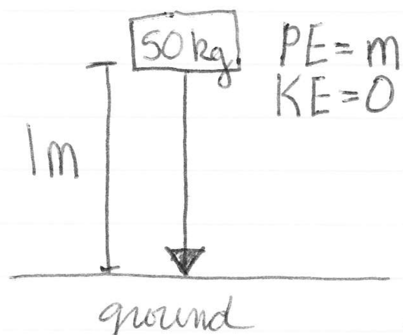
HW 1 Key

16: 1, 5, 16
19: 1, 4, 19, 24, 36, 41, 48

① Stuff with Units:

$$R = 0.0821 \frac{L \cdot atm}{K \cdot mole} \times \frac{0.26417\,gal}{1\,L} \times \frac{14.6959\,PSI}{1\,atm} = \boxed{0.31873 \frac{gal \cdot psi}{K \cdot mol}}$$

② ⓐ



$PE = m \cdot g \cdot h$, $KE = 0$ } at 1 m

$PE = 0$, $KE = \frac{mv^2}{2}$ } at the ground (just before impact)

$\Delta PE = PE(\text{at } 0m) - PE(\text{at } 1m)$

$\Delta PE = 0 - (50\,kg)(9.81\,m\,s^{-2})(1m)$

$\boxed{\Delta PE = -490.5\,kg\,m^2 s^{-2} = -490.5\,J}$

Note: Negative b/c PE is lost to KE during the fall.

Ⓑ $1\,g\,C \times \frac{1\,mole\,C}{12\,g\,C} \times \frac{393\,kJ}{1\,mole\,C} \times \frac{1000\,J}{1\,kJ} = \boxed{32{,}750\,J \text{ released}}$

$C + O_2 \rightarrow CO_2$, $q = -393\,kJ/mole$ (negative b/c heat was released)

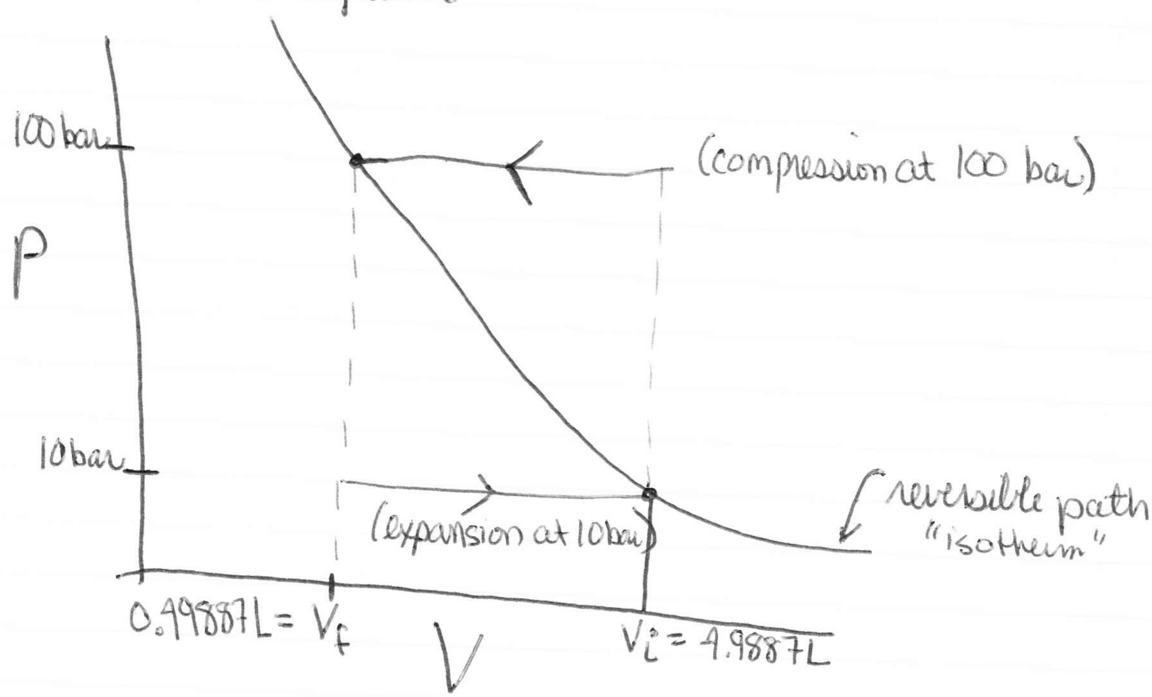
Ⓒ $1840\,Cal \times \frac{1\,kcal}{1\,Cal} \times \frac{1000\,cal}{1\,kcal} \times \frac{4.184\,J}{1\,cal} = \boxed{7.70 \times 10^6\,J}$

Ⓓ $100\,W = 100\,\frac{J}{s} \times 1\,day \times \frac{24\,hrs}{1\,day} \times \frac{3600\,s}{1\,hr} = \boxed{8.64 \times 10^6\,J}$

③ 1^{st} Law: $\Delta U = q + w$

→ For an ideal gas: $\Delta U = n C_{v,m} \Delta T$ (only changes in T can change U for an ideal gas)

An indicator diagram:



Isothermally means $\Delta T = 0$.

Compression Step: $\Delta U_c = q_c + w_c$ (C subscript means "compression")

$\Delta U_c = 0\,J$ (b/c $\Delta T = 0$)

$q_c = -w_c$

Formal def^{n} of work: $w = -\int_{V_i}^{V_f} p(V)\,dV$

For ideal gas, p[redacted] $= \frac{nRT}{V}$ (equation of state)

Find V_f, V_i using IGL: $V_f = \frac{(2)(0.083145\ L \cdot bar \cdot K^{-1} mol^{-1})(300K)}{100\ bar}$

$V_f = 0.49887\,L$

$V_i = 4.9887\,L$

If done at cons. pressure, integral becomes:

$$w = -p_{ex}\int_{V_i}^{V_f} dV = -p_{ex}(V_f - V_i) = -p_{ex}\Delta V$$

Where pex is the external pressure at which process is carried out.

$$W_c = -(100 \text{ bar})(0.48997\,L - 4.8997\,L)$$
$$W_c = 440.97 \text{ bar}\cdot L = 44{,}097\text{ J}$$

$$\Delta U_c = 0 \quad (\text{b/c } \Delta T = 0)$$
$$\Delta U_c = 0 = q_c + w_c$$
$$w_c = -q_c$$
$$q_c = -44{,}097\text{ J}$$

Expansion step: Same as above but $p_{ex} = 10$ bar, $V_f = 4.8997L$, and $V_i = 0.48997L$.

$$\Delta U_e = w_e + q_e \quad (\text{e subscript is for expansion})$$
$$0 = w_e + q_e$$
$$q_e = -w_e$$

$$w_e = -p_{ex}\Delta V = -(10\text{ bar})(4.8997\,L - 0.48997\,L)$$
$$w_e = -44.097 = -4{,}409.8\text{ J}$$
$$q_e = +4{,}409.8\text{ J}$$

irreversible process

For both steps
$$\Delta U_{TOT} = \Delta U_c + \Delta U_e = 0\text{ J} + 0\text{ J} = 0\text{ J}$$
$$W_{TOT} = 44{,}097\text{ J} - 4{,}409.8\text{ J} = 39{,}687.2\text{ J}$$
$$q_{TOT} = -39{,}687.2\text{ J}$$

For reversible process, $p = \frac{nRT}{V}$ + plugged into work equation

$$w_c = -\int_{4.9887L}^{0.49987L} \frac{nRT}{V}\, dV$$

n, R, T are constants that come out of integral:

$$w_c = -nRT \int_{4.9887L}^{0.49987L} \frac{1}{V}\, dV$$

$$w_c = -nRT \ln V \Big|_{4.9887L}^{0.49987L}$$

$$w_c = -(2\,mol)(0.083145\ bar \cdot L \cdot mol^{-1} \cdot K^{-1})(300K) \ln\left(\frac{0.49987L}{4.9887L}\right)$$

$$w_c = 114.87\ L \cdot bar = 11{,}487\ J$$

(w is ⊕ b/c this is compression)

$$\Delta U_c = 0J = 11{,}487J + q_c$$

$$q_c = -11{,}487J$$

Do the same thing for expansion step, except that now $V_i = 0.49887L$ and $V_f = 4.9887L$.

$\Delta U_e = q_e + w_e$ (e subscript denotes expansion)

$$w_e = -nRT \ln\left(\frac{4.9887L}{0.49887L}\right) = -11{,}487J$$

$$q_e = +11{,}487J$$

So for total process: $\Delta U_{TOT} = 0J$, $q_{TOT} = 0J$, $w_{TOT} = 0J$ ← reversible process

④ Bertholet Equation: $P = \frac{nRT}{V-nb} - \frac{n^2a}{TV^2}$

$$\text{Work} = -\int_{V_i}^{V_f} p(V)\,dV$$

reversible means p(V) will be set to p at all stages of the process.

$$\text{work} = -\int_{4L}^{10L} \frac{nRT}{V-nb}\,dV + \int_{4L}^{10L} \frac{n^2a}{TV^2}\,dV$$

Isothermal means T is constant, so n, R, T, a can come out of integral:

$$\text{work} = -nRT\int_{4L}^{10L} \frac{1}{V-nb}\,dV + \frac{n^2a}{T}\int_{4L}^{10L} \frac{1}{V^2}\,dV$$

$$\text{work} = -nRT\ln(V-nb)\Big|_{4L}^{10L} - \frac{n^2a}{T}(V^{-1})\Big|_{4L}^{10L}$$

$$\text{work} = -(2\,\text{mol})(0.083145\,\tfrac{\text{bar L}}{\text{K mol}})(300\,\text{K})\cdot\ln\left(\frac{10L-(2\,\text{mol})(0.0427\,L\cdot\text{mol}^{-1})}{4L-(2\,\text{mol})(0.0427\,L\cdot\text{mol}^{-1})}\right)$$

$$-\frac{(2\,\text{mol})^2(1080\,L^2\,\text{bar}\,K\,\text{mol}^{-2})}{(300\,K)}\left(\frac{1}{10L}-\frac{1}{4L}\right)$$

don't forget the sign!

$\text{work} = -46.3597\ \text{bar}\cdot L + 2.16\ \text{bar}\cdot L =$ L·bar $=$
$-44.199\ L\cdot\text{bar} = \boxed{-4{,}419.9\ J}$

$\Delta U = nC_{V,m}\Delta T$ is only valid for an ideal gas. The Berthelot Eqn represents a real gas. ΔU will be a fxn of both V and T, so the method for solution will be more complex. If you can get ΔU, you have w + have q.

⑤ $$C_p = C_v + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Compute partial derivatives first:

$$P = \frac{nRT}{V-nb}$$

$$\left(\partial P/\partial T\right)_V = \frac{nR}{V-nb}$$

$$V = \frac{nRT}{P} + nb$$

$$\left(\partial V/\partial T\right)_P = \frac{nR}{P}$$

$$C_p = C_v + T\left(\frac{nR}{V-nb}\right)\left(\frac{nR}{P}\right)$$

$$C_p = C_v + \frac{Tn^2R^2}{nRT}$$

$$\boxed{C_p = C_v + nR}$$

⑦ Data for Rxn:

at 298K

$\Delta H_f^\circ (Na_{(s)}) = 0 \text{ kJ mol}^{-1}$ $C_p(Na_{(s)}) = 28.24 \text{ J K}^{-1}\text{mol}^{-1}$

$\Delta H_f^\circ (H_2O_{(l)}) = -285.83 \text{ kJ mol}^{-1}$ $C_p(H_2O_{(l)}) = 75.291 \text{ J K}^{-1}\text{mol}^{-1}$

$\Delta H_f^\circ (H_{2(g)}) = 0 \text{ kJ mol}^{-1}$ $C_p(H_{2(g)}) = 28.824 \text{ J K}^{-1}\text{mol}^{-1}$

$\Delta H_f^\circ (Na^+_{(aq)}) = -240.12 \text{ kJ mol}^{-1}$ $C_p(Na^+_{(aq)}) = 46.4 \text{ J K}^{-1}\text{mol}^{-1}$

$\Delta H_f^\circ (OH^-_{(aq)}) = -229.99 \text{ kJ mol}^{-1}$ $C_p(OH^-_{(aq)}) = -148.5 \text{ J K}^{-1}\text{mol}^{-1}$

$$2\,Na_{(s)} + 2\,H_2O_{(l)} \longrightarrow H_{2(g)} + 2\,Na^+_{(aq)} + 2\,OH^-_{(aq)}$$

$$\Delta_r H^\circ(298) = \sum_{\text{products}} \nu_j \Delta_f^\circ H_j - \sum_{\text{reactants}} \nu_i \Delta_f^\circ H_i$$

$$\Delta_r H^\circ(298) = (1)\Delta_f^\circ H_{(H_2)} + (2)\Delta_f^\circ H_{(Na^+)} + (2)\Delta_f^\circ H_{(OH^-)} - 2\Delta_f^\circ H_{(Na)} - 2\Delta_f^\circ H_{(H_2O)}$$

$$\Delta_r H^\circ(298) = (1)(0\ kJ/mol) + (2)(-240.12\ kJ/mol) + (2)(-229.99\ kJ/mol) - (2)(0\ kJ/mol) - (2)(-285.83\ kJ/mol)$$

$$\Delta_r H^\circ(298) = \frac{-368.56\ kJ}{2\ mole\ Na} = \boxed{-184.28\ kJ/mol}$$

$$\Delta_r H^\circ(350) = \Delta_r H^\circ(298) + \Delta C_p \Delta T,\ \text{where}\ \Delta C_p = \sum_{\text{products}} \nu_j C_{p,j} - \sum_{\text{reactants}} \nu_i C_{p,i}$$

$$\Delta_r H^\circ(350) = -184\ kJ/mol + (350-298)K \cdot [(1)(28.824) + (2)(96.4) + (2)(-148.5) - (2)(28.24) - (2)(75.291)]\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_r H^\circ(350) = -184\ kJ/mol + \frac{(350-298)K \cdot (-382.438\ J \cdot K^{-1} \cdot mol^{-1})}{2\ mole\ Na}$$

$$\Delta_r H^\circ(350) = -184\ kJ/mol - 9.94\ kJ/mol$$

$$\boxed{\Delta_r H^\circ(350) = -193.9\ kJ/mol}$$

10 g Na @ 298K:

$$10\ g\ Na \times \frac{1\ mole\ Na}{23\ g\ Na} \times \frac{-184.28\ kJ}{1\ mole\ Na} = \boxed{-80.12\ kJ} = q_{298}$$

10 g Na @ 350K:

$10 g\ Na \times \frac{1\ mole\ Na}{23 g\ Na} \times \frac{-193.9\ kJ}{1\ mole\ Na} = \boxed{-84.3\ kJ} = q_{398}$

Work - For chemical rxn, treat gases as ideal. Can derive an expression for the work:

$$W = -\Delta n_g RT$$

where Δn_g is the change in the # of moles of gas ($n_{f,gas} - n_{i,gas}$)

$W_{298} = -(1-0)(8.3145)\ J \cdot K^{-1} \cdot mol^{-1} \cdot$ [illegible] $(298K)$

$\boxed{W_{298} =}$ [illegible] $\boxed{-2.47\ kJ}$

$W_{350} = -(1-0)(8.3145\ J/K \cdot mol)(350K)$

$\boxed{W_{350} = -2.91\ kJ}$

A 50 K increase in T causes the reaction to be more exothermic by ~10 kJ while the change in the work is about 0.5 kJ. [illegible]