

SOLUTIONS

PROBLEM SET 2

CHM 3400, Dr. Chatfield

- 3.4** A 7.24-g sample of ethane occupies 4.65 L at 294 K. **(a)** Calculate the work done when the gas expands isothermally against a constant external pressure of 0.500 atm until its volume is 6.87 L. **(b)** Calculate the work done if the same expansion occurs reversibly.

(a)

$$w = -P_{\text{ex}}\Delta V = -(0.500 \text{ atm})(6.87 \text{ L} - 4.65 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -112 \text{ J}$$

(b)

$$w = -nRT \ln \frac{V_2}{V_1} = -\frac{7.24 \text{ g}}{30.07 \text{ g mol}^{-1}} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (294 \text{ K}) \ln \frac{6.87 \text{ L}}{4.65 \text{ L}} = -230 \text{ J}$$

Note that work done in the reversible process in **(b)** is greater in magnitude than that in the irreversible process in **(a)**.

- 3.8** Some driver's test manuals state that the stopping distance quadruples as the velocity doubles. Justify this statement by using mechanics and thermodynamic arguments.

The kinetic energy of a moving vehicle is given by $E_{\text{kin}} = \frac{1}{2}mv^2$. If the velocity doubles, the kinetic energy quadruples. If $v_2 = 2v_1$, then $E_2 = \frac{1}{2}m(2v_1)^2 = 4E_1$. Assuming kinetic energy is dissipated at a constant rate in the brakes and between the tires and the road as heat through friction, then the stopping distance is proportional to the energy. The doubling in velocity quadruples the kinetic energy and thus the stopping distance.

- 3.10** An ideal gas is compressed isothermally by a force of 85 newtons acting through 0.24 meter. Calculate the values of ΔU and q .

$\Delta U = 0$ for an ideal gas undergoing an isothermal process. Using this information, q can be calculated from w , the work done on the system.

$$w = (\text{force})(\text{distance}) = (85 \text{ N})(0.24 \text{ m}) = 20 \text{ J}$$

Because $\Delta U = 0 = q + w$, $q = -w = -20 \text{ J}$.

- 3.14** An ideal gas is compressed isothermally from 2.0 atm and 2.0 L to 4.0 atm and 1.0 L. Calculate the values of ΔU and ΔH if the process is carried out **(a)** reversibly and **(b)** irreversibly.

ΔU and ΔH of an ideal gas depend only on ΔT . Therefore, for any isothermal process [either process **(a)** or **(b)**], $\Delta U = 0$ and $\Delta H = 0$.

- 3.22 A 10.0-g sheet of gold with a temperature of 18.0°C is laid flat on a sheet of iron that weighs 20.0 g and has a temperature of 55.6°C . Given that the specific heats of Au and Fe are $0.129\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$ and $0.444\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$, respectively, what is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (*Hint*: The heat gained by the gold must be equal to the heat lost by the iron.)

The final temperature of the sheet of gold is the same as that of the sheet of iron when thermal equilibrium is reached, and is denoted by T_f . Furthermore, the amount of heat gained by gold is the same as that lost by iron, that is,

$$q_{\text{Au}} = -q_{\text{Fe}}$$

The “-” sign is used to indicate that q_{Au} and q_{Fe} are of opposite sign.

The above relation gives

$$\begin{aligned} m_{\text{Au}}s_{\text{Au}}\Delta T_{\text{Au}} &= -m_{\text{Fe}}s_{\text{Fe}}\Delta T_{\text{Fe}} \\ (10.0\text{ g}) (0.129\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}) (T_f - 18.0^\circ\text{C}) &= -(20.0\text{ g}) (0.444\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}) (T_f - 55.6^\circ\text{C}) \\ (1.29\text{ J }^\circ\text{C}^{-1}) (T_f - 18.0^\circ\text{C}) &= -(8.88\text{ J }^\circ\text{C}^{-1}) (T_f - 55.6^\circ\text{C}) \\ T_f - 18.0^\circ\text{C} &= -\frac{8.88\text{ J }^\circ\text{C}^{-1}}{1.29\text{ J }^\circ\text{C}^{-1}} (T_f - 55.6^\circ\text{C}) \\ &= -6.884 (T_f - 55.6^\circ\text{C}) \\ &= -6.884T_f + 382.8^\circ\text{C} \\ 7.884T_f &= 400.8^\circ\text{C} \\ T_f &= 50.8^\circ\text{C} \end{aligned}$$

- 3.32 The equation of state for a certain gas is given by $P [(V/n) - b] = RT$. Obtain an expression for the maximum work done by the gas in a reversible isothermal expansion from V_1 to V_2 .

Write P in terms of n , V , and T :

$$P = \frac{RT}{\frac{V}{n} - b} = \frac{nRT}{V - nb}$$

The maximum work done by the gas undergoing an isothermal expansion is

$$\begin{aligned} w &= -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \frac{nRT}{V - nb} dV \\ &= -nRT \ln(V - nb) \Big|_{V_1}^{V_2} \\ &= -nRT \ln \frac{V_2 - nb}{V_1 - nb} \end{aligned}$$

- 3.36** A 0.1375-g sample of magnesium is burned in a constant-volume bomb calorimeter that has a heat capacity of $1769 \text{ J } ^\circ\text{C}^{-1}$. The calorimeter contains exactly 300 g of water, and the temperature increases by 1.126°C . Calculate the heat given off by the burning magnesium, in kJ g^{-1} and in kJ mol^{-1} .

Heat given off by the burning magnesium is absorbed by the calorimeter and water. The heat absorbed is calculated using the heat capacity of the calorimeter, specific heat of water, and the temperature rise.

$$\begin{aligned}\text{Heat gained by calorimeter and water} &= (1769 \text{ J } ^\circ\text{C}^{-1}) (1.126^\circ\text{C}) \\ &\quad + (300 \text{ g}) (4.184 \text{ J g}^{-1} ^\circ\text{C}^{-1}) (1.126^\circ\text{C}) \\ &= 3.405 \times 10^3 \text{ J}\end{aligned}$$

Therefore, heat given off by the magnesium is

$$\frac{3.405 \times 10^3 \text{ J}}{0.1375 \text{ g}} = 2.48 \times 10^4 \text{ J g}^{-1} = 24.8 \text{ kJ g}^{-1}$$

or

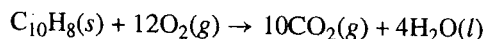
$$(2.48 \times 10^4 \text{ J g}^{-1}) (24.31 \text{ g mol}^{-1}) = 6.03 \times 10^5 \text{ J mol}^{-1} = 603 \text{ kJ mol}^{-1}$$

- 3.39** When 1.034 g of naphthalene (C_{10}H_8) are completely burned in a constant-volume bomb calorimeter at 298 K, 41.56 kJ of heat is evolved. Calculate the values of $\Delta_r U$ and $\Delta_r H$ for the reaction.

Since volume is constant, $w = 0$, and therefore,

$$\Delta_r U = q = \frac{-41.56 \text{ kJ}}{(1.034 \text{ g}) \left(\frac{1 \text{ mol}}{128.16 \text{ g}}\right)} = -5151.2 \text{ kJ mol}^{-1} = -5151 \text{ kJ mol}^{-1}$$

The change in number of moles of gases needs to be determined before $\Delta_r H$ can be evaluated. From the combustion of 1 mole of naphthalene,



$\Delta n = 10 - 12 = -2$. Thus,

$$\begin{aligned}\Delta_r H &= \Delta_r U + RT \Delta n = -5151.2 \text{ kJ mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) (-2) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -5156 \text{ kJ mol}^{-1}\end{aligned}$$

- 3.62 Predict whether the values of q , w , ΔU , ΔH are positive, zero, or negative for each of the following processes: (a) melting of ice at 1 atm and 273 K, (b) melting of solid cyclohexane at 1 atm and the normal melting point, (c) reversible isothermal expansion of an ideal gas, and (d) reversible adiabatic expansion of an ideal gas.

For most substances, the volume increases upon melting, but for ice melting to water under the conditions given, the volume decreases. In all cases, the volume change between the solid and liquid phases is small as is the value of the work associated with the melting. For ideal gases, both internal energy, U , and enthalpy, H , depend only on temperature. Keeping these points in mind results in the following predictions.

	q	w	ΔU	ΔH
(a)	positive	positive	positive	positive
(b)	positive	negative	positive	positive
(c)	positive	negative	zero	zero
(d)	zero	negative	negative	negative

- 3.80 An ideal gas is isothermally compressed from P_1 , V_1 to P_2 , V_2 . Under what conditions would the work done be a minimum? A maximum? Write the expressions for minimum and maximum work done for this process. Explain your reasoning.

The conditions are opposite to those for the isothermal *expansion* of an ideal gas. The minimum work is done in an reversible process because the opposing (internal) pressure is only infinitesimally smaller than the external pressure causing the compression. The work done under these conditions is

$$w_{\min} = -nRT \ln \frac{V_2}{V_1}$$

Since $V_2 < V_1$, the work is positive as expected for a compression.

The maximum work would be done in an irreversible process and an external pressure of P_2 , giving a value of

$$w_{\max} = -P_2 (V_2 - V_1)$$

- 3.82 State whether each of the following statements is true or false: (a) $\Delta U \approx \Delta H$ except for gases or high-pressure processes. (b) In gas compression, a reversible process does maximum work. (c) ΔU is a state function. (d) $\Delta U = q + w$ for an open system. (e) C_V is temperature independent for gases. (f) The internal energy of a real gas depends only on temperature.

(a) True (b) False (c) False (U is a state function, ΔU is not.) (d) False (It is true for a *closed* system.) (e) False (f) False

- 3.90 From your knowledge of heat capacity, explain why hot, humid air is more uncomfortable than hot, dry air and cold, damp air is more uncomfortable than cold, dry air.

As a non-linear, triatomic molecule, H_2O has more rotational motions (3 versus 2) than the two diatomic molecules, N_2 and O_2 , that comprise the bulk of air. This leads to a larger heat capacity for water compared to the other molecules, which means that more energy is required to effect a given temperature change. Thus, hot, humid air with its greater content of water vapor, is capable of transferring more thermal energy to your body than the diatomic gases, making hot, humid air more uncomfortable than hot, dry air. (Of course, the retardation of the evaporation rate from your skin is another significant reason.) On the other hand, the greater water content in cold damp air is more able to remove thermal energy from your body than cold, dry air can.

- 3.84 Derive an expression for the work done during the isothermal, reversible expansion of a van der Waals gas. Account physically for the way in which the coefficients a and b appear in the final expression. [Hint: You need to apply the Taylor series expansion:

$$\ln(1-x) = -x - \frac{x^2}{2} \dots \quad \text{for } |x| \ll 1$$

to the expression $\ln(V-nb)$. Recall that the a term represents attraction and the b term repulsion.]

$$\begin{aligned} w &= - \int_{V_1}^{V_2} P \, dV \\ &= - \int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2} \right) dV \\ &= -nRT \ln \frac{V_2-nb}{V_1-nb} - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

The \ln term can be written as

$$\begin{aligned}
\ln \frac{V_2 - nb}{V_1 - nb} &= \ln \frac{V_2 \left(1 - \frac{nb}{V_2}\right)}{V_1 \left(1 - \frac{nb}{V_1}\right)} \\
&= \ln \frac{V_2}{V_1} + \ln \frac{1 - \frac{nb}{V_2}}{1 - \frac{nb}{V_1}} \\
&= \ln \frac{V_2}{V_1} + \ln \left(1 - \frac{nb}{V_2}\right) - \ln \left(1 - \frac{nb}{V_1}\right)
\end{aligned}$$

Assume the volume occupied by the gas molecules is much greater than the volume of the molecules, both before and after the expansion, that is, $V_1 \gg nb$ and $V_2 \gg nb$, then $\frac{nb}{V_1} \ll 1$ and $\frac{nb}{V_2} \ll 1$. Under these condition, the Taylor expansion described in the question can be used to simplify the \ln terms.

$$\begin{aligned}
\ln \frac{V_2 - nb}{V_1 - nb} &= \ln \frac{V_2}{V_1} + \left(-\frac{nb}{V_2} - \frac{1}{2} \frac{n^2 b^2}{V_2^2} + \dots\right) - \left(-\frac{nb}{V_1} - \frac{1}{2} \frac{n^2 b^2}{V_1^2} + \dots\right) \\
&= \ln \frac{V_2}{V_1} - nb \left(\frac{1}{V_2} - \frac{1}{V_1}\right) - \frac{n^2 b^2}{2} \left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) + \dots
\end{aligned}$$

Substitute the above expression into w .

$$\begin{aligned}
w &= -nRT \left[\ln \frac{V_2}{V_1} - nb \left(\frac{1}{V_2} - \frac{1}{V_1}\right) - \frac{n^2 b^2}{2} \left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) + \dots \right] - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right) \\
&= -nRT \ln \frac{V_2}{V_1} + (bRT - a) n^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \frac{n^3 b^2 RT}{2} \left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) + \dots
\end{aligned}$$

The first term in this last equation is just the result for the ideal gas. It is modified by the succeeding terms to account for intermolecular interactions. The second term shows the balance between attractive and repulsive forces. In an expansion, $V_2 > V_1$ so $\left(\frac{1}{V_2} - \frac{1}{V_1}\right) < 0$. If attractive forces dominate, $a > bRT$ and the entire second term is positive, which cancels some of the (negative) work done in the expansion. Because of the attractive forces, some energy must be used to overcome the intermolecular interactions, and not as much work can be done as in the case of the ideal gas.

On the other hand, if $a < bRT$, the entire second term is negative and enhances the (negative) work done in the expansion. In this case the repulsive forces dominate, and the energy released as the molecules move farther apart from each other is available to do more work than the ideal gas could. The higher order terms reinforce this effect for high densities where the repulsive forces are most significant.