Experiment 3. Heat-Capacity Ratios for Gases. Adiabatic Expansion Method

Background

For the reversible adiabatic expansion of a perfect gas, the change in energy content is related to the change in volume by

$$dE = -pdV = -\frac{nRT}{V}dV = -nRTd\ln V \tag{4}$$

Since E for a perfect gas is a function of temperature only, we can also write $dE = C_v dT$. Substituting this expression into Eq. (4) and integrating, we find that

$$\widetilde{C}_v \ln\frac{T_2}{T_1} = -R\ln\frac{\widetilde{V}_2}{\widetilde{V}_1} \tag{5}$$

where $\widetilde{C}_v$ and $\widetilde{V}$ are molar quantities (that is, C_v/n, V/n). We assumed here that C_v is constant over the temperature range involved. Eq. (5) predicts the decrease in temperature resulting from reversible adiabatic expansion of a perfect gas.

In experiment, we will use the following two-step process involving a perfect gas denoted by A:

Step I: Allow the gas to expand adiabatically and reversibly until the pressure has dropped from p_1 to p_2:

$$A\left(p_1,\widetilde{V}_1,T_1\right) \to A\left(p_2,\widetilde{V}_2,T_2\right) \tag{6}$$

Step II: At constant volume, restore the temperature of the gas to T_1:

$$A\left(p_2,\widetilde{V}_2,T_2\right) \to A\left(p_3,\widetilde{V}_2,T_1\right) \tag{7}$$

For step I, we can use the perfect-gas law to obtain

$$\frac{T_2}{T_1} = \frac{p_2\widetilde{V}_2}{p_1\widetilde{V}_1} \tag{8}$$

Substituting Eq. (8) into Eq. (5) and combining terms in $\widetilde{V}_2/\widetilde{V}_1$, we can write

$$\ln\frac{p_2}{p_1} = \frac{-\left(\widetilde{C}_v + R\right)}{\widetilde{C}_v}\ln\frac{\widetilde{V}_2}{\widetilde{V}_1} = -\frac{\widetilde{C}_p}{\widetilde{C}_v}\ln\frac{\widetilde{V}_2}{\widetilde{V}_1} \tag{9}$$

since for a perfect gas

$$\widetilde{C}_p = \widetilde{C}_v + R \tag{10}$$

For step II, which restores the temperature to T_1,

$$\frac{\widetilde{V}_2}{\widetilde{V}_1} = \frac{p_1}{p_3} \tag{11}$$

Thus

$$\ln\frac{p_1}{p_2} = \frac{\widetilde{C}_p}{\widetilde{C}_v}\ln\frac{p_1}{p_3} \tag{12}$$

This can be rewritten in the form

$$\gamma \equiv \frac{\widetilde{C}_p}{\widetilde{C}_v} = \frac{\ln(p_1/p_2)}{\ln(p_1/p_3)} \tag{13}$$

The goal of our experiment is to obtain γ for two gases, N_2 and Ar, through measurements of p_1, p_2, and p_3.

Experimental procedure

See Fig. 2 in p. 109 of Shoemaker's textbook. The change in state (6) is carried out by quickly removing and replacing the stopper of a large carboy containing the desired gas at a pressure initially somewhat higher than 1 atm pressure, so that the pressure of gas in the carboy (p_1) momentarily drops to atmospheric pressure p_2. The change in state (7) consists of allowing the gas remaining in the carboy to return to its initial temperature. The initial pressure p_1 and the final pressure p_3 are read from an open-tube manometer.

The apparatus should be assembled as shown in Fig. 2. The manometer is an open-tube manometer, one side of which is open to the atmosphere; the pressure that it measures is therefore the difference of pressure from atmospheric pressure. The atmospheric pressure in the lab should measured using a barometer. The liquid in the manometer is dibutyl phthalate, which has a density of 1.046 g cm^{-3} at room temperature (20ºC). To convert manometer readings (millimeters of dibutyl phthalate) to equivalent readings in millimeters of mercury, multiply by the ratio of this density to the density of mercury, which is 13.55 g cm^{-3} at 20ºC. To find the total pressure in the carboy, the converted manometer readings should be added to atmospheric pressure as given by a barometer.

1) Seat the rubber stopper firmly in the carboy and open the clumps on tubes *a* and *b*. Clamp off the tube *c*. The connections shown in Fig. 2 are based on the assumption that the gas to be studied is heavier than air (or the previous gas in the carboy) and therefore should be introduced at the bottom in order to force the lighter gas out at the top; in the event that the gas to be studied is lighter, the connections *a* and *b* should be reversed.
2) Allow the gas to be studied to sweep through the carboy for ~15 min. The rate of gas flow should be about 6 L min^{-1}, 100 mL s^{-1}. Measure this rate roughly in an inverted beaker held under water in the thermostat bath. Five volumes of gas (90 L) will pass through the carboy.
3) Retard the gas flow to a fraction of the flushing rate by partly closing the clamp on tube *a*. *Carefully* open the clamp *c*, and then cautiously (to avoid blowing liquid out of the manometer) clamp off the exit the exit tube *b*, keeping a close watch on the manometer. When the manometer has attained a reading of about 600 mm of oil, clamp off tube *a*. Allow the gas to come to the ambient temperature (about 15 min or less), as will be indicated by a constant manometer reading. Record this reading; when it is converted to an equivalent mercury reading and added to the barometer reading, p_1 is obtained.
4) Remove the stopper entirely (at a distance of 2 or 3 in.) from the carboy, and replace it *in the shortest possible time*, making sure that it is tight. As the gas warms back up to the ambient temperature, the pressure will increase and finally (in about 15 min) reach a new constant value p_3, which can be determined from the manometer reading and the barometer reading. At some point of the procedure, a barometer reading (p_2) should be taken as well as an ambient temperature reading.
5) Repeat the steps above to obtain two more determinations with the same gas. For these repeated runs, long flushing is not necessary; one additional volume of gas should suffice to check the effectiveness of the original flushing.

Measurements are to be made on argon and nitrogen.

Calculations

For each of three runs on Ar and N_2, calculate $\widetilde{C}_p / \widetilde{C}_v$ using Eq. (13). Also calculate the theoretical value of $\widetilde{C}_p / \widetilde{C}_v$ predicted by the equipartition theorem (see below). In the case of N_2, calculate the ratio both with and without a vibrational contribution to $\widetilde{C}_v$ of R per vibrational degree of freedom. Assuming that all the gases can be treated as ideal and thus $\widetilde{C}_p = \widetilde{C}_v + R$, obtain approximate values for the molar constant-volume heat capacity $\widetilde{C}_v$ for Ar and N_2.

Results expected from theory

Using classical statistical mechanics, one can derive the theorem of the equipartition of energy. According to this theorem, $kT/2$ of energy is associated with each quadratic term in the expression for the energy. Thus, there is associated with each translational or rotational degree of freedom for a molecule a contribution to the energy of $kT/2$ of kinetic energy and for each vibrational degree of freedom a contribution of $kT/2$ of kinetic energy and $kT/2$ of potential energy. (The corresponding contributions to the energy per mole of gas are $RT/2$.)

A monoatomic gas has no rotational or vibrational energy but does have a translational energy of $\frac{3}{2}RT$ per mole. The constant-volume heat capacity of a monoatomic gas is thus

$$\widetilde{C}_v = \left(\frac{\partial \widetilde{E}}{\partial T}\right)_V = \frac{3}{2}R$$

For diatomic or polyatomic molecules, we can write

$$\widetilde{E} = \widetilde{E}(trans) + \widetilde{E}(rot) + \widetilde{E}(vib)$$

The equipartition theorem is based on classical mechanics. Its application to translational motion is in accord with quantum mechanics as well. At ordinary temperatures the rotational results are also in accord with quantum mechanics. The vibrational energy is however highly quantized and depends strongly on temperature: the various vibrational modes are at ordinary temperatures only partially “active” and the degree of activity strongly depends on temperature. The lower the vibrational frequency, the more "active" is a given degree of freedom at a given temperature and the greater is the contribution to the heat capacity. In the case of most gaseous diatomic molecules (where the one vibrational mode is pure stretch), the vibrational contribution to $\widetilde{C}_v$ is very small: for example, N_2 would have its classical equipartition value for $\widetilde{C}_v$ only above about 4000 K.

For polyatomic molecules, theory based on the equipartition theorem allows one to calculate only limiting values of $\widetilde{C}_v$ by either completely ignoring all vibrational contributions or assuming that the vibrational contributions achieve their full classical value. For monoatomic gases and all ordinary diatomic molecules (where the vibrational contribution is not important at room temperature and can be ignored),† definite $\widetilde{C}_v$ values can be calculated.

For a given $\widetilde{C}_v$ value, the ratio $\widetilde{C}_p / \widetilde{C}_v$ for a perfect gas is given by

$$\gamma \equiv \frac{\widetilde{C}_p}{\widetilde{C}_v} = 1 + \frac{R}{\widetilde{C}_v}$$

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† According to quantum mechanics, contribution of the vibrational degree of freedom to $\widetilde{C}_v$ of a diatomic molecule can be calculated using its vibrational frequency $\widetilde{\nu}$:

$$\widetilde{C}_v(vib) = R\frac{u^2 e^{-u}}{\left(1 - e^{-u}\right)^2}$$

where $u = h\nu / kT = hc\widetilde{\nu} / kT = 1.4388\widetilde{\nu} / T$

(See Experiment 37, p. 407 in the textbook for detail).

Experiment 6. Heats of combustion

Background: principles of calorimetry

Our goal in this experiment is to determine the enthalpy change ΔH or the energy change ΔE accompanying a given isothermal change in state of a system, in which a chemical reaction occurs:

$$\mathrm{A}(T_0) + \mathrm{B}(T_0) = \mathrm{C}(T_0) + \mathrm{D}(T_0) \qquad (1)$$

If n is the number of moles of the limiting reagent, the molar quantities for the reaction are $\Delta\widetilde{H} = \Delta H / n$ and $\Delta\widetilde{E} = \Delta E / n$.

In practice we do not actually carry out the change in state isothermally; this is not necessary because ΔH and ΔE are independent of the path. In calorimetry it is convenient to use a path composed of two steps:

Step I. A change in state is carried out adiabatically in the calorimeter vessel to yield the desired products but in general in another temperature:

$$\mathrm{A}(T_0) + \mathrm{B}(T_0) + \mathrm{S}(T_0) = \mathrm{C}(T_1) + \mathrm{D}(T_1) + \mathrm{S}(T_1) \qquad (2)$$

where S represents those parts of the system (e.g., inside wall of the calorimeter vessel, stirrer, thermometer, solvent) that are always at the same temperature as the reactants or products because of the experimental arrangement; these parts, plus the reactants or products, constitute the system under discussion.

Step II. The products of step I are brought to the initial temperature T_0 by adding heat to (or taking it from) the system:

$$\mathrm{C}(T_1) + \mathrm{D}(T_1) + \mathrm{S}(T_1) = \mathrm{C}(T_0) + \mathrm{D}(T_0) + \mathrm{S}(T_0) \qquad (3)$$

It is often unnecessary to carry out this step in actuality, since the associated change in energy or enthalpy can be calculated from the known temperature difference.

By adding Eqs. (2) and (3), we obtain Eq. (1) and verify that these two steps describe a complete path connecting the desired initial and final states. Accordingly, ΔH or ΔE for the change in state (1) is the sum of values of this quantity pertaining to the two steps:

$$\Delta H = \Delta H_{\mathrm{I}} + \Delta H_{\mathrm{II}} \qquad (4a)$$

$$\Delta E = \Delta E_{\mathrm{I}} + \Delta E_{\mathrm{II}} \qquad (4b)$$

The particular convenience of the path described is that the heat q for step I is zero, while the heat q for step II can be either measured or calculated. It can be measured directly by carrying out step II (or its inverse) through the addition to the system of a measurable quantity of heat or electrical energy, or it can be calculated from the temperature change ($T_1 - T_0$) resulting from adiabatic step I if the heat capacity of the product system is known. For step I,

$$\Delta H_\mathrm{I} = q_p = 0 \qquad \text{constant pressure} \qquad (5a)$$

$$\Delta E_\mathrm{I} = q_v = 0 \qquad \text{constant volume} \qquad (5a)$$

Thus, if both steps are carried out at constant pressure,

$$\Delta H = \Delta H_\mathrm{II} \qquad (6a)$$

and if both steps are carried out at constant volume,

$$\Delta E = \Delta E_\mathrm{II} \qquad (6b)$$

The determination of a heat of combustion is conveniently carried out at constant volume in a “bomb calorimeter”. We can easily calculate ΔH from ΔE as determined from a constant-volume process by use of the equation

$$\Delta H = \Delta E + \Delta(pV) \qquad (7)$$

When gases are involved, as in the gase of combustion, the $\Delta(pV)$ term is likely to be significant in magnitude, though still small in comparison with ΔH or ΔE. Since it is small, we can employ the perfect gas law and rewrite Eq. (7) in the form

$$\Delta H = \Delta E + RT\Delta n_\mathrm{gas} \qquad (8)$$

where Δn_gas is the *increase* in the number of moles of gas in the system.

It is often not necessary to actually carry out step II. If we know or can determine the heat capacity of the system, the temperature change ($T_1 - T_0$) resulting from step I provides all the additional information we need:

$$\Delta H_{II} = \int_{T_1}^{T_0} C_p(C + D + S)dT \qquad (11a)$$

$$\Delta E_{II} = \int_{T_1}^{T_0} C_v(C + D + S)dT \qquad (11b)$$

The heat capacities vary only slightly over the small temperature ranges involved: accordingly we can simplify Eqs. (11) and combine them with Eqs. (6) to obtain

$$\Delta H = -C_p(C + D + S)(T_1 - T_0) \qquad (12a)$$

$$\Delta E = -C_v(C + D + S)(T_1 - T_0) \qquad (12b)$$

where C_p and C_v are average values over the temperature range.

The heat capacity must be determined if it is not known. An indirect method of determining the heat capacity is to carry out another reaction all together, for which the heat of reaction is known, in the same calorimeter under the same conditions. This method depends on the fact that in most calorimetric measurements on chemical reactions the heat capacity contributions of the actual product species (C and D) are very small, and often negligible, in comparison with the contribution due to the parts of the system denoted by the symbol S. In a bomb-calorimeter experiment the reactants or products amount to a gram or two, while the rest of the system is the thermal equivalent of about 2.5 kg of water. Thus, we may write, in place of Eqs. (12a) and (12b),

$$\begin{matrix}\Delta H \\ \Delta E\end{matrix} = -C(S)(T_1 - T_0) \qquad (14)$$

The value of C(S) can be calculated from the heat of the known reaction and the adiabatic temperature change $(T_2' - T_1')$ produced by it, as follows:

$$C(\mathrm{S}) = \begin{cases} \dfrac{-\Delta H_{known}}{T_2' - T_1'} & \text{constant pressure} \qquad (15a) \\[2ex] \dfrac{-\Delta E_{known}}{T_2' - T_1'} & \text{constant volume} \qquad (15b) \end{cases}$$

Now we consider step I, the adiabatic step, and the measurement of the temperature difference ($T_1 - T_0$), which is the fundamental measurement of calorimetry. If this step could be carried out in an *ideal* adiabatic calorimeter, the temperature variation would look like Fig. 1a (see p. 148 of your textbook). In this case there would be no difficulty in determining the temperature change $\Delta T = T_1 - T_0$, since $(dT/dt) = 0$ before the time of mixing the reactants and after the products achieve thermal equilibrium. The only cause of the temperature change here is the chemical reaction. However, it is unrealistic idealization to assume that step I is truly adiabatic; as no thermal insulation is perfect, some heat will in general leak into or out the system during the time required for the change in state to occur and for the thermometer to come into equilibrium with the product system. In addition, we have a stirrer present in the calorimeter to hasten thermal equilibration. The mechanical work done on the system by the stirrer results in the continuous addition of the energy to the system at a small, approximately constant rate. During the time period required for the change in state and thermal equilibration to occur, the amount of energy introduced can be significant. A typical temperature-time variation is shown in Fig. 1b (p. 148) and a more detailed analysis is needed to extract the adiabatic ΔT value from the observed data points. The initial temperature T_i is taken to be the value at time t_i when the reaction is initiated following a period of essentially linear T, t readings that serve to establish the initial (prereaction) drift rate $(dT/dt)_i$. The temperature is followed after the reaction for a period long enough to achieve a roughly linear variation and to establish the drift rate $(dT/dt)_f$ at an arbitrary point T_f,t_f. The effect of heat leakage is evaluated using Newton's law of cooling,

$$\frac{dq}{dt} = -k\left(T - T_s\right) \tag{16}$$

where T_s is the temperature of the surroundings (air temperature in the laboratory) and k is a thermal rate constant that depends on thermal conductivity of the calorimeter insulation. The mechanical power input to the system (dw/dt) is denoted by P and assumed to be a constant independent of t. Thus

$$C_v \frac{dT}{dt} = \frac{dE}{dt} = P - k\left(T - T_s\right) \tag{17}$$

or

$$\left(\frac{dT}{dt}\right)_{leak+stir} = \frac{1}{C_v}\left[P - k\left(T - T_s\right)\right] \tag{18}$$

The temperature difference $T_f - T_i$ shown in Fig. 2 (p. 149) is given by

$$T_f - T_i = \Delta T + \int_{t_i}^{t_f} \left(\frac{dT}{dt}\right)_{leak+stir} dt \tag{19}$$

where $\Delta T = T_1 - T_0$ is the change to an adiabatic chemical reaction and the integral is the net change due to the heat leak and stirrer power input. Thus it follows that

$$T_1 - T_0 \equiv \Delta T = \left(T_f - T_i\right) - \frac{1}{C}\int_{t_i}^{t_f} \left\{P - k\left[T(t) - T_s\right]\right\} dt \tag{20}$$

The calorimeter is built in such a way as to minimize heat conduction into or out of the system. We may assume that the rate of gain or loss of energy by the system resulting from heat leakage and stirrer work is reasonably constant with time at any given temperature and therefore the temperature variation as a function of time should be initially and finally almost linear. One simple possibility would be $k(T - T_s) = 0$ and $P =$ constant, in which case $(dT/dt) = P/C$ has the same value at all $t < t_i$ and $t > t_f$ and

$$\Delta T = T_f - T_i - \frac{dT}{dt}\left(t_f - t_i\right) \qquad \text{if } k\left(T - T_s\right) = 0 \tag{21}$$

As shown in Fig. 3a (p. 150), ΔT in this case is just the vertical distance between two parallel T-t lines and this distance can be evaluated at any t.

A more realistic possibility is that $k(T - T_s)$ is small but not negligible and $P =$ constant. In this case, the T-t plot looks like Fig. 3b (p. 150), where the initial leak + stir rate $(dT/dt)_i$ at t_i differs from the final rate $(dT/dt)_f$ at t_f. It can be shown (see p. 151) that

$$\Delta T = \left(T_f - T_i\right) - \left(\frac{dT}{dt}\right)_i \left(t_d - t_i\right) - \left(\frac{dT}{dt}\right)_f \left(t_f - t_d\right) \tag{22}$$

where t_d is chosen so that the two shaded regions in Fig. 3b are of equal area.

In summary, on should follow the temperature variation before and after the reaction for a period long enough to allow a good evaluation of $(dT/dt)_i$ and $(dT/dt)_f$. Then make a plot like Fig. 3b, choose the point (T_f,t_f), determine the best value for t_d, and calculate ΔT from Eq. (22). In practice t_f should be chosen as close to t_i as is consistent with a well characterized final drift rate. Note that t_d will lie much closer to t_i that to t_f for reactions that go to completion quickly.

Experimental procedure

In this experiment a bomb calorimeter is employed in the determination of the heat of combustion of naphthalene, $C_{10}H_8$. The heat of combustion of naphthalene is $-\Delta\widetilde{H}$ for the reaction at constant temperature and pressure:

$$C_{10}H_8(s) + 12O_2(g) = 10CO_2(g) + 4H_2O(l)$$

Following the procedure given below, three runs should be made with benzoic acid to determine the heat capacity of the calorimeter, and three runs should be maid with naphthalene.

Condition of apparatus. The bomb must be clean and dry, with no bits of iron left on the terminals. It is recommended to polish lightly those electric terminals with emery paper. Make sure that the jacket is completely empty and that all switches on the control box are off. Check to see that the inside of the calorimeter is dry.

Filling the bomb.

1) Cut the iron wire, free from sharp bends or kinks, to the correct length and weigh it accurately.
2) Press pellets of the substance concerned, of mass 0.5 ± 0.1 g for naphthalene and 0.8 ± 0.1 g for benzoic acid. Shave them to the desired mass with a knife or spatula if necessary.
3) Install the pellet and wire in the bomb. The pellet should be on the wire, and the wire should touch only the terminals. Carefully assemble the bomb and screw down the cap hand-tight.
4) Attach the bomb to the oxygen-filling apparatus. *Carefully* open the main supply valve on the oxygen cylinder and *slowly* fill the bomb to 380 psi. **Do not exceed 450 psi.** Release the pressure to flush out most of the atmospheric nitrogen originally present in the bomb. Refill the bomb to 380 psi. Check the bomb for leaks by immersing it in water. If a leak does exist, vent the bomb, loosen and rotate the head slightly, and then retighten the screw cap. An occasional bubble – one every 5 or 10 s – is inconsequential.

Assembly of calorimeter.

1) Dry the bomb and set it in the dry pail. Then set the pail in the calorimeter, making sure it is centered and does not touch the inner wall of the jacket. Make the electrical connection to the top of the bomb and be sure it is tight.
2) Fill a 2-L volumetric flask with water at 25°C (use both hot and cold water; add the two as required, swirling and checking with a thermometer until the flask is almost full, then make up to the mark. Pour the water from the flask into the pail; avoid splashing. Allow the flask to drain for about 30 s.
3) Put the calorimeter lid in place and clamp the precision thermometer in place as low as it will go without obscuring the scale. The temperature of the pail should be within half a degree of 25°C.

4) With all switches off, plug the stirrer and ignition cords into the control box. Recheck the wiring and then plug the control box into a 110-V outlet. Turn on the stirrer and make sure it runs smoothly.

Making the run.

1) Begin time-temperature readings, reading the precision thermometer every 30 s and recording both the time and temperature. Estimate the temperature to thousandths of a degree if feasible. Tap the thermometer *gently* before each reading. *Do not interrupt the time-temperature readings until the run is over*. The calorimeter pail temperature should change at avery slow linear rate (of the order of 0.001 K min^{-1}). After this steady rate has persisted for at least 5 min, the bomd may be ignited.
2) To ignite, turn the ignition switch on and then immediately off. Record the exact time. The burning wire will ignite the pellet, and after a period of 10 or 15 s the temperature will begin to rise. After a few minutes the pail temperature should again show a slow, steady rate of change. Do not discontinue readings; continue them until the time since ignition has been at least four times the period required for attainment of this steady rate. The purpose of this is to provide a valid basis for extrapolation. When readings are completed, turn all switches off.
3) Disassemble the apparatus, release the bomb pressure, and open the bomb. Remove and weigh any unburned iron wire. Subtract the weight of unburned iron wire from the initial iron-wire weight to obtain the net weight of iron burned. If the inside of the bomb is found to be coated with soot, the amount of oxygen present at the time of ignition was presumably insufficient to give complete combustion and the run should be discarded. Wipe dry all bomb parts.

Calculations

For each run, plot temperature versus time using an expanded, interrupted temperature scale as shown in Fig. 1b (p. 148) and determine the initial and final drift rates $(dT/dt)_i$ and $(dT/dt)_f$. Then make and overall T versus t plot like Fig. 3b (p. 150), choose t_f, and determine t_i and t_d. The "adiabatic" temperature change $\Delta T \equiv T_1 - T_0$ can be calculated from Eq. (22).

The heat capacity $C(\mathrm{S})$ is found by determining the adiabatic temperature rise $(T_2' - T_1')$ obtained in the combustion of a known mass of benzoic acid (and a known mass of iron wire) using Eq. (15b). For calculating the energy change produced, the specific (i.e., per gram) energies of combustion of benzoic acid and iron wire given below can be used:

$$\Delta\overline{E}_{BA} = -26.41 \text{ kJ g}^{-1} \qquad \Delta\overline{E}_{Fe} = -6.68 \text{ kJ g}^{-1}$$

Then, ΔE for the combustion of a weighted specimen of naphthalene is determined from the rise in temperature $(T_1 - T_0)$ and the heat capacity $C(\mathrm{S})$ by use of Eq. (14). The value of ΔE obtained includes a contribution for the combustion of iron wire; this must be subtracted to yield the contribution from the naphthalene alone. The molar energy change $\Delta\widetilde{E}$ is then obtained by dividing the number of moles of the reactant that is present in the least equivalent amount (in this case, naphthalene). The molar enthalpy change $\Delta\widetilde{H}$ can be then obtained by use of Eq. (8).

Report the individual and average values of the heat capacity $C(\mathrm{S})$ and the individual and average values of the molar enthalpy change $\Delta\widetilde{H}$ for the combustion of naphthalene, calculated using the average $C(\mathrm{S})$.

Experiment 13. Vapor pressure of a pure liquid

Background

When a pure liquid is placed in an evacuated bulb, molecules will leave the liquid phase and enter the gas phase until the pressure of vapor in the bulb reaches a definite value, which is determined by the nature of the liquid and its temperature. This pressure is called the vapor pressure of the liquid at a given temperature. The equilibrium vapor pressure is independent of the quantity of liquid and vapor present, as long as both phases exist in equilibrium with each other at the specified temperature. As themperature is increased, the vapor pressure also increases up to the critical point, at which the two-phase system becomes a homogeneous, one-phase fluid.

If the pressure above the liquid is maintained at a fixed value, then the liquid may be heated up to a temperature at which the vapor pressure is equal to the external pressure. At this point vaporization will occur by the formation of bubbles in the interior of the liquid as well as at the surface; this is the boiling point of the liquid at the specified external pressure. Clearly, the temperature of the boiling point is a function of the external pressure; in fact, about a given T,p point, the variation of the boiling point with external pressure is the inverse of the variation of the vapor pressure with temperature.

In this experiment the variation of vapor pressure for water with temperature will be measured and used to determine the molar heat of vaporization.

We deal here with the equilibrium between a pure liquid and its vapor:

$$X(l) = X(g) \qquad (p,T) \tag{1}$$

A definite relationship exists between the values of p and T at equilibrium, as given by

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \tag{2}$$

for an equilibrium system composed of a pure substance with both phases always present. ΔS and ΔV refer to the change in entropy and volume when one phase transforms to the other at constant p and T. Since the change in state (1) is isothermal and ΔG is zero, ΔS may be replaced by $\Delta H/T$. The results is

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \tag{3}$$

Equation (2) or (3) is known as the *Clapeyron equation*. It is an exact equation that may be applied to phase equilibria of all kinds. Since the heat of vaporization ΔH_v is positive and ΔV is positive for vaporization, the vapor pressure must increase with increasing temperature.

For the case of vapor-liquid equilibria in the range of vapor pressures less than 1 atm, one may assume that the molar volume of the liquid $\widetilde{V}_l$ is negligible in comparison with that of the gas $\widetilde{V}_g$, so that $\Delta\widetilde{V} = \widetilde{V}_g$. This assumption is very good in the low-pressure region, since $\widetilde{V}_l$ is usually only a few tenths of a percent of $\widetilde{V}_g$. Thus we obtain

$$\frac{dp}{dT} = \frac{\Delta\widetilde{H}_v}{T\widetilde{V}_g} \tag{4}$$

Since $d \ln p = dp/p$ and $d(1/T) = -dT/T^2$, we can rewrite Eq. (4) in the form

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta\widetilde{H}_v}{R}\frac{RT}{p\widetilde{V}_g} = -\frac{\Delta\widetilde{H}_v}{RZ} \tag{5}$$

where we have introduced the *compressibility factor Z* for the vapor:

$$Z = \frac{p\widetilde{V}_g}{RT} \tag{6}$$

Eq. (5) is a convenient form of the Clapeyron equation. We can see that, if the vapor were perfect gas ($Z \equiv 1$) and $\Delta\widetilde{H}_v$ were independent of temperature, then a plot of $\ln p$ versus $1/T$ would be a straight line, the slope of which would determine $\Delta\widetilde{H}_v$. Indeed, for many liquids, $\ln p$ is almost a linear function of $1/T$, which implies at least that $\Delta\widetilde{H}_v / Z$ is almost constant.

Considering the question of gas imperfections, in general, Z decreases as the temperature increases. However, water, owing to its high critical temperature, is a reasonably ideal gas even at 100ºC, where Z equals 0.986. Next we must consider the variation of $\Delta\widetilde{H}_v$ with temperature. For a change of state such as in Eq. (1),

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT + \int_{p_1}^{p_2} \left(\frac{\partial \Delta H}{\partial p}\right)_T dp \tag{7}$$

Since $\left(\partial H_g / \partial p\right)_T$ is zero for a perfect gas and very small for most real gases and $\left(\partial H_l / \partial p\right)_T$ is always very small for liquids, we can neglect the final term and approximate Eq. (7) by

$$\Delta H_{T_2} \cong \Delta H_{T_1} + \overline{\Delta C_p}\left(T_2 - T_1\right) \tag{8}$$

where $\overline{\Delta C_p}$ is the average value over the temperature interval. For $\Delta \widetilde{H}_v$ to be independent of temperature, the average value of $\overline{\Delta \widetilde{C}_p}$ must be very close to zero, which is generally not true (see Table 1 in p. 202). In general the value of $\Delta \widetilde{H}_v$ will decrease as the temperature increases. Since both $\Delta \widetilde{H}_v$ and Z decrease with increasing temperature, it is possible to see why $\Delta \widetilde{H}_v / Z$ might be almost constant, yielding a nearly linear plot of $\ln p$ versus $1/T$.

Experimental procedure: Boiling point method

A common method of measuring the vapor pressure as a function of temperature is one in which the variation of the boiling point with external applied pressure is measured. The total pressure above the liquid can be varied and maintained at a given value by use of a large volume ballast bulb; this pressure is then measured with a mercury manometer. The liquid to be studied (water) is heated until boiling occurs, and the temperature of the refluxing vapor is measured in order to avoid any effects of superheating. The apparatus is assembled as shown in Fig. 2 (see p. 203).

1) Use pressure tubing to connect the condenser and the manometer to the ballast bulb. Fill the flask about one-third full with water. A few carborundum boiling chips should be added to reduce “bumping”. Be sure that the thermometer scale is visible over a range of at least 50ºC below the boiling point at 1 atm. Also, make sure that the thermometer bulb is positioned carefully so that the temperature of coexisting vapor and liquid is measured. Heating should be accomplished with an electrical heating mantle. Turn on the circulating water to the condenser before heating the liquid, and turn it off at the end of the experiment.
2) Use the manometer with the greatest care; be careful not to allow liquid to condense in it. Stopcock X should be open only when the manometer is to be read

and closed immediately after each reading. Stopcock *X* should not be open at the same time as stopcock *S* is open, either to vacuum or to the air.

3) To make a reading, adjust the heating so as to attain steady boiling of the liquid, but avoid heating it too strongly. When conditions appear to be steady, open stopcock *X* carefully and watch the manometer. When manometer and thermometer appear to be steady as they can be maintained, read them as nearly simultaneously as possible. The thermometer should be read to the nearest 0.1ºC, and vapor should be condensing on and dripping from the thermometer bulb to ensure that the equilibrium temperature is obtained. In reading the manometer, record the position of each meniscus (h_1 and h_2), keeping your line of sight level with the meniscus to avoid parallax error. Estimate your readings to the nearest 0.1 mm. Record the ambient air temperature at the manometer several times during the run.
4) To change the pressure in the system between the measurements, first remove the heating mantle, then check to make sure that stopcock *X* is closed. After a short time, admit some air or remove some air by opening stopcock S for a few seconds. Be especially careful in removing air from the ballast bulb to avoid strong bumping. Then open stopcock *X* carefully to measure the pressure with the manometer. Repeat as often as necessary to attain the desired pressure. Close stopcock *X* and restore the heating mantle to its position under the flask.
5) Take readings at approximately the following pressures:
   Pressure descending: 90, 110, 140, 180, 230, 300, 400, 520, 670 Torr
   Pressure ascending: 760, 600, 450, 350, 260, 200, 160, 130, 100, 80 Torr

Calculations

Correct all manometer pressure readings ($h_2 - h_1$) for the fact that mercury is not at 0ºC by multiplying by ($1 - 1.8\text{x}10^{-4}t$), where t is the Celsius temperature of the manometer. If t has been reasonably constant during experiment, use an average value and apply the same correction factor to all pressures.

Convert all Celsius temperature readings to absolute temperatures T and plot $\ln p$ versus $1/T$. If there is no systematic curvature, draw the best straight line through the points. If there is noticeable curvature, draw a smooth curve through the points and also draw a straight line tangent to the curve at about the midpoint. Determine the slope of the straight line of tangent. From Eq. (5) it follows that this slope is $\Delta\widetilde{H}_v / RZ$.

In addition to this graphical analysis, carry out a least-squares fit to your p-versus-T data. If visual inspection of your ln p-versus-$1/T$ plot does not indicate any systematic curvature, make a direct line fit of ln p as a function of $1/T$. If systematic curvature is observed, make a least squares fit of ln p with the empirical power-series form $a + b/T + c/T^2$. Then differentiate the resulting expression to obtain $\Delta\widetilde{H}_v / RZ$.

Report both the graphical and the least-squares values of $\Delta\widetilde{H}_v / Z$. Estimate the value of Z for the saturated vapor at the appropriate temperature from Fig. 1 (p. 201) and calculate $\Delta\widetilde{H}_v$ in J mol $^{-1}$. Report the value of the heat of vaporization and the vapor pressure for the liquid at the applicable temperature (corresponding to the midpoint of the range studied).