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Chapter 2

The First Law of Thermodynamics

- **2.2.** Work is defined as *negative* $p\Delta V$ because if a system does work on the surroundings, the system *loses* energy.
- **2.4.** $1780 \text{torr} \left| \frac{1 \text{atm}}{} \right| = 2.34 \text{atm}$ (760 torr)

$$w = -P\Delta V = -2.34 atm (1.00L - 3.55L) \left(\frac{101.32J}{1L \cdot atm} \right) = +605J$$

605 J of work are done ON the system.

- **2.6.** (a) The work would be less because the external pressure is less.
 - (b) The work would be greater because the external pressure is greater.
 - (c) No work would be performed because the external pressure is (effectively) zero.
- **2.8.** First, we need to find the final volume of the CO_2 . Using $P_1V_1 = P_2V_2$, we find that $V_2 = 105 \text{mL}$

$$w = -(1.0atm)(105 - 25.0mL) \left(\frac{1L}{1000mL}\right) \left(\frac{101.32J}{1L \cdot atm}\right) = -8.1J$$

2.10. First, determine the ΔT : 330 K – 298 K = 32 K.

Using
$$q = m \cdot c \cdot \Delta T$$
, we rearrange: $c = \frac{q}{m \cdot \Delta T}$

Substituting:
$$c = \frac{288 \text{ J}}{(50.5 \text{ g})(32 \text{ K})} = 0.178 \frac{\text{J}}{\text{g} \cdot \text{K}}$$
.

2.12. First, we need to calculate the number of moles of phosphorous:

(

$$50.0g P \left(\frac{1 \text{mole}}{30.97 g}\right) = 1.61 \text{molesP}$$

$$q = \begin{cases} (1.61 \text{moles}) & 56.99 + 0.1202T \\ \int & \text{mol} \cdot K \end{cases} dT$$

$$q = 1.61 \text{moles} \left[56.99T + \frac{0.1202T}{2} \right]_{298}^{350} = 8.03 \times 10^{3} J$$

2.14. The kinetic energy of the hailstone, KE, is equal to:

$$\frac{1}{2} \text{mv}^2 = \frac{1}{2} (6.0 \times 10^{-5} \text{kg}) (10.0 \text{m/s})^2 = 3.0 \times 10^{-3} \text{J}$$

Since all of the kinetic energy is converted into thermal energy, we can say that: $KE = m \cdot c \cdot \Delta T$

$$3.0 \times 10^{-3} J = \left(6.0 \times 10^{-2} g\right) \left(2.06 \frac{J}{g \cdot K}\right) (\Delta T)$$

$$\Delta T = 0.024 K$$

2.16. First, calculate the energy needed to warm the water by 1.00°C:

$$q = m \cdot c \cdot \Delta T = (1.00 \times 10^5 \text{ g})(4.18 \text{ J/g} \cdot \text{K})(1.00 \text{ K}) = 4.18 \times 10^5 \text{ J}$$

Now, determine how many drops of a 20.0 kg weight falling 2.00 meters in gravity will yield that much energy. The amount of energy in one drop is

$$mgh = (20.0 \text{ kg})(9.81 \text{ m/s}^2)(2.00 \text{ m}) = 392.4 \text{ J. Therefore,}$$

drops =
$$\frac{4.18 \times 10^5 \text{ J}}{392.4 \text{ J/drop}} = 1065 \text{ drops}.$$

- **2.18.** True. As the gas expands, the average distance between molecules increases. For a real gas, work must be done to increase this distance due to intermolecular attractive forces between the gas molecules.
- **2.20.** The major inaccuracy is the omission of the phrase "for an isolated system", since for non-isolated systems energy can move in or out, giving the impression that that energy is created and/or destroyed. Can you find other inaccuracies?
- **2.22.** q = -124.0 J

$$w = -p_{ext}\Delta V = -(1550 \text{ torr})(119 \text{ mL} - 377)$$
 $\frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = +0.526 \text{ L} \cdot \text{atm}$

$$w = +0.526 \text{ L} \cdot \text{atm} \times \frac{101.32 \text{ J}}{1 \text{ L} \cdot \text{atm}} = +53.3 \text{ J}$$

Since
$$\Delta U = q + w$$
, $\Delta U = -124.0 \text{ J} + 53.3 \text{ J}$ $\Delta U = -70.7 \text{ J}$

2.24. Reversibly:
$$w = -nRT \ln \frac{V_f}{V_i} = -(1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(298.0 \text{ K}) \ln \frac{10 \text{ L}}{1.0 \text{ L}} = -5705 \text{ J}$$

Irreversibly:
$$w = -p_{ext}\Delta V = -(1.00 \text{ atm})(10\text{L} - 1.0 \text{ L}) \times \frac{101.32 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -912 \text{ J}$$

The reversible work is much larger than the irreversible work. This is one numerical example of the concept that the maximum amount of work is obtained by a reversible process.

2.26. If any change in a system is isothermal, then the change in U must be zero. It doesn't matter if the process is adiabatic or not!

- **2.28.** Of the two distances mentioned, the 9-mile distance between the two cities is analogous to a state function, because that distance is independent of how a trip is actually traveled between the two cities.
- **2.30.** The keys to this problem are the stated conditions. If the processes are adiabatic, then q = 0. If the initial and final temperatures are the same, then $\Delta U = 0$. By the first law of thermodynamics, if ΔU and q are 0, then w = 0 as well. While these values fit the conditions of the problem, do you think that a piston can even work under such conditions? Probably not.
- **2.32.** First, we should determine the number of moles of gas in the cylinder. Assuming the ideal gas law holds:

$$pV = nRT$$
 can be rearranged to $n = \frac{pV}{RT} = \frac{(172 \text{ atm})(80.0 \text{ L})}{(0.08205 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(20.0 + 273.15 \text{ K})}$

 $n = 572 \text{ mol N}_2 \text{ gas}$

(a) The final pressure can be determined using Charles' law: $\frac{p_i}{T_i} = \frac{p_f}{T_f}$

$$p_f = \frac{p_i T_f}{1} = \frac{(172 \text{ atm})(140.0 + 273.15 \text{ K})}{1} = 242 \text{ atm}$$

$$T_i$$
 (20.0 + 273.15 K) p_f

(b) w = 0 since the volume of the tank does not change.

$$q = n \cdot \Delta T = (572 \text{ mol})(21.0 \text{ J/mol·K})(140.0^{\circ}\text{C} - 20.0^{\circ}\text{C}) = 1.44 \times 10^{6} \text{ J}$$

 $\Delta U = q + w = 1.44 \times 10^{6} \text{ J} + 0 = 1.44 \times 10^{6} \text{ J}.$

2.34.
$$w = -nRT \ln \frac{V_f}{V_i} = -(0.505 \text{ mol})(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(5.0 + 273.15 \text{ K}) \ln \frac{0.10 \text{ L}}{1.0 \text{ L}} = +2689 \text{ J}$$

$$q = -2690 \text{ J (given)}$$

$$\Delta U = q + w = -2690 \text{ J} + 2689 \text{ J} = -1 \text{ J}$$

 $\Delta H = \Delta U + \Delta(pV)$ Since the process occurs at constant temperature, Boyle's law applies and $\Delta(pV) = 0$. Therefore, $\Delta H = -1$ J.

2.36. Since we're at the normal boiling point, the vaporization is a constant-pressure process (1 atm at the normal boiling point). Therefore, $\Delta H = q_p$ and $\Delta H = +2260$ J/g.

For work, we need change in volume. Assuming the ideal gas law holds, the volume of 1 gram of steam at 100°C (373.15 K) is:

$$n = 1 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 0.0555 \text{ mol}$$

$$V = \frac{nRT}{p} = \frac{(0.0555 \text{ mol})(0.08205 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(373.15 \text{ K})}{0.988 \text{ atm}} = 1.720 \text{ L}$$

The volume of a gram of water, 1.00 mL, is negligible compared to this. Therefore, let us use $\Delta V = 1.720$ L. Therefore:

$$w = -(0.988 \text{ atm})(1.720 \text{ L}) \times \frac{101.32 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -172 \text{ J}$$

Since $\Delta U = q + w$, we have $\Delta U = +2260 \text{ J} - 172 \text{ J} = 2088 \text{ J}$.

2.38. In terms of pressure and volume: $dU = \left(\frac{\partial U}{\partial p}\right)_V dp + \left(\frac{\partial U}{\partial V}\right)_p dV$.

For enthalpy:
$$dH = \left(\frac{\partial H}{\partial p}\right)_V dp + \left(\frac{\partial H}{\partial V}\right)_p dV$$
.

2.40. $w = -P\Delta V = 0$; There is no change in volume. Assuming the heat capacity of an ideal gas:

$$\Delta U = q = \int_{348.45}^{298.15} \frac{1}{nC_{v}} dT = \int_{348.45}^{298.15} (35.0g) \left(\frac{1mole}{2.016g} \right) \left(\frac{J}{20.78} \right) dT = \left(\frac{J}{361} \right) \left(\frac{J}{K} \right) T \Big|_{348.45}^{298.15} = -1.82 \times 10^{4} J$$

Using the ideal gas law:

$$\Delta H = \Delta U + \Delta (PV) = \Delta U + V \Delta P = \Delta U + V \begin{pmatrix} nR\Delta T \\ V \end{pmatrix}$$

$$= -1.82 \times 10^{4} J + (35.0g) \left(\frac{1mole}{2.016g}\right) \left(8.314 \frac{J}{K \cdot mol}\right) (298.15 - 348.45K) = -2.55 \times 10^{4} J$$

2.42.
$$q = m \cdot s \cdot \Delta T = (244g) \begin{pmatrix} 4.184 & J \\ K \cdot mol \end{pmatrix} (20.0 - 80.0K) = -6.13 \times 10^4 J$$

Since it is a constant pressure process (assumed 1 atm), ΔH =-6.13x10⁴J.

Now, we need to calculate the volume change of the coffee:

$$\Delta V = \Delta \left| \frac{mass}{density} \right| = (244g) \left| \frac{1cm}{0.9982g} - \frac{1cm}{0.9718g} \right| = -6.64cm^3$$

$$w = -P\Delta V = -(1atm)(-6.64cm^3) \left(\frac{1mL}{cm^3}\right) \left(\frac{1L}{1000mL}\right) \left(\frac{101.32J}{1L \cdot atm}\right) = 0.673J$$

$$\Delta U = q + w = -61300J + 0.67J = -6.13 \times 10^4 J$$

2.44. Start with $\overline{\Delta U} = \overline{C}_V \Delta T$ and $\overline{\Delta H} = \overline{\Delta U} + \Delta \left(p \overline{V} \right)$: Since $p \overline{V} = RT$ for an ideal gas, we also have $\overline{\Delta H} = \overline{\Delta U} + \Delta \left(RT \right)$. Substituting for $\overline{\Delta H}$ (equation 2.32) and $\overline{\Delta U}$ (equation 2.27): $\overline{C}_v \Delta T = \overline{C}_v \Delta T + \Delta (RT)$

R is a constant, so it can be removed from the Δ term:

$$\overline{C}_{p}\Delta T = \overline{C}_{v}\Delta T + R\Delta T$$

Now all terms can be divided by ΔT to get the desired relationship:

$$\overline{C}_{p} = \overline{C}_{v} + R$$
.

- **2.46.** isobaric = constant pressure isochoric = constant volume isenthalpic = constant enthalpy isothermal = constant temperature. A gaseous system that has all these conditions simultaneously probably isn't undergoing any physical change! Can you conceive of a process in which *all* of these conditions are satisfied at once?
- **2.48.** Actually, the ideal gas law *can* be used to determine the Joule-Thomson coefficient for an ideal gas, but it will turn out that the Joule-Thomson coefficient for an ideal gas is zero!
- **2.50.** Using the approximate version $\mu_{JT} = \frac{\Delta T}{\Delta p}$:

 $\Delta p = 0.95 \text{ atm} - 200.00 \text{ atm} = -199.05 \text{ atm Since } \mu_{JT} = 0.150 \text{ K/atm}$:

$$0.150 \text{ K/atm} = \frac{\Delta T}{-199.05 \text{ atm}}$$
 $\Delta T = (0.150 \text{ K/atm})(-199.05 \text{ atm}) = -29.9 \text{ K}$

If the initial temperature is 19.0° C and the temperature drops by 29.9 degrees, the final temperature should be about $19.0 - 29.9 = -10.9^{\circ}$ C.

2.52. μ_{JT} for Argon at 0°C and 1atm is 0.4307K/atm. From Eqn 2.35 we know that:

2.54. Although ΔU and ΔH have similar behavior for isothermal processes of ideal gases, they won't necessarily for real gases. Therefore, a Joule-Thomson coefficient defined in terms of U can be defined but will not have the same numerical value as one defined in terms of U. In addition, the Joule-Thomson experiment is originally defined (as is μ_{JT}) for an

isenthalpic process, not one for which U is constant. Therefore, that definition of μ_{JT} would probably not be proper.

2.56. Since
$$\overline{C}_V = \frac{3}{2}R$$
 and $\overline{C}_p = \frac{5}{2}R$:

$$\frac{3}{2}R = \frac{3}{2}(8.314 \text{ J/mol} \cdot \text{K}) \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 2.981 \text{ cal/mol} \cdot \text{K}$$

Or, in different units: $\frac{3}{2}(0.08205 \text{ L} \cdot \text{atm/mol} \cdot \text{K}) = 0.1231 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$

$$\frac{5}{2}R = \frac{5}{2}(8.314 \text{ J/mol} \cdot \text{K}) \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 4.968 \text{ cal/mol} \cdot \text{K}$$

Or, in different units: $\frac{5}{2}(0.08205 \text{ L} \cdot \text{atm/mol} \cdot \text{K}) = 0.2051 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$

- **2.58.** \overline{C}_V for a monatomic ideal gas is equal to $\frac{3}{2}R$. Using the equation $\Delta U = w = n\overline{C}_V\Delta T$: -75 $J = (0.122 \text{ mol})(12.47 \text{ J/mol} \cdot \text{K}) \cdot \Delta T$ and solve for ΔT : $\Delta T = -49 \text{ K}$. Since the initial temperature was 235°C = 508 K, the final temperature is 508 -49 = 459 K.
- **2.60.** $\gamma = \frac{\overline{C}_p}{C_v}$. For a monatomic ideal gas, $\gamma = \frac{\left(\frac{5R}{2}\right)}{2} = \frac{5}{2}$
- **2.62.** (a) CO₂ is a linear polyatomic molecule where N=3 atoms. In the low temperature limit it only has contributions from translational and rotational motion so

$$\overline{C}_V = \frac{3}{R} + R = \frac{5}{R}. \ \overline{C}_P = \frac{7}{R}, \text{so } \gamma = \frac{C_P}{C_V} = \frac{7}{2}. \text{ In the high temperature limit,}$$

vibrational motion contributes as well so:

$$\overline{C}_{V} = \frac{5}{R} R + (3N - 5)R = \frac{13}{R} R. \overline{C}_{P} = \frac{15}{R}, \text{so } \gamma = \frac{\overline{C}_{P}}{C} = \frac{15}{R}$$

(b) H_2O is a non-linear polyatomic molecule where N=3 atoms. In the low temperature limit it only has contributions from translational and rotational motion so

$$\overline{C}_{_V}=\frac{3}{}R+\frac{3}{}R=3R.$$
 $\overline{C}_{_P}=4R,$ so $\gamma=\frac{C_{_P}}{}=\frac{4}{}$. In the high temperature limit,

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$$\overline{C}_V = 3R + (3N - 6)R = 6R$$
. $\overline{C}_P = 7R$, so $\gamma = \frac{\overline{C}_P}{C_V} = \frac{7}{6}$

2.64. Using Eqn. 2.47:
$$\left(\frac{V_{i}}{V_{f}}\right)^{2/3} = \frac{T_{f}}{T_{i}}$$

$$\left(\begin{array}{c} \\ \\ \\ \\ \\ \end{array}\right)^{2/3} \\ \left(\begin{array}{c} \\ \\ \\ \\ \end{array}\right)^{2/3} \\ = \frac{x}{;} \quad x = 0.63T \; ; \quad \text{The final temperature is 63\% of the initial temperature.} \\ \left(\begin{array}{c} \\ \\ \\ \\ \end{array}\right)^{i} \quad T_{i}$$

Therefore, the absolute temperature will drop to 55% of its initial temperature.

- **2.68.** As vibrational energies begin to have more significance, γ decreases. As γ decreases, the exponent in the equation in Example 2.14 become smaller. This makes the final temperature in the second example higher than the first as is demonstrated.
- **2.70.** (a) N_2 and CO have nearly identical molar masses, M. What is different between the two gases is γ over a temperature range. By measuring the speed of sound at several different temperatures of the gases, one should be able to differentiate between the two.
 - (b At 100K:

$$speed = \sqrt{\frac{7 \parallel 8.314 \frac{J}{\parallel 100K}}{5 \frac{K \cdot mol}{\parallel 100K}}} = 163 \text{m/s}$$

$$\sqrt{\frac{0.04401 \frac{\text{kg}}{\text{mol}}}{100K}}$$

At 500 K:

speed =
$$\sqrt{\frac{\frac{15}{\parallel 8.314} \frac{J}{\parallel 500K}}{\frac{(13) \frac{1}{\parallel 6.314} \frac{K \cdot mol}{\parallel 6.04401} \frac{kg}{mol}}} = 330 \text{m/s}$$

2.72. The volumes of both water and ice at 0°C are:

water:
$$V_1 = \frac{18.02 \text{ mL}}{0.99984 \text{ g/mL}} = 18.02 \text{ mL}$$
; ice: $V_s = \frac{19.66 \text{ mL}}{0.9168 \text{ g/mL}} = 19.66 \text{ mL}$.

Therefore, $\Delta V = 19.66 \text{ mL} - 18.92 \text{ mL} = 0.74 \text{ mL}$, so that the work is

$$w = -p_{ext}\Delta V = -(1bar) \left(\frac{1atm}{1.01325bar} \right) \times (0.74mL) \left(\frac{1L}{1000mL} \right) \left(\frac{101.32J}{11.000mL} \right) = -0.074J.$$

2.74. According to Table 2.3, 1 gram of H₂O gives up 2260 J when it condenses. Since each gram of ice requires 333.5 J to melt, we get

$$2260 \text{ J} \times \frac{1 \text{ g}}{333.5 \text{ J}} = 6.78 \text{ grams of ice that can be melted.}$$

2.76.
$$\Delta_{rxn}H = \sum \Delta_f H(\text{prods}) - \sum \Delta_f H(\text{rcts}) = (2 \text{ mol})(26.5 \text{ kJ/mol}) - 0 - 0 = 53.0 \text{ kJ}$$

2.78.
$$\Delta_{\text{rxn}} H = 60\Delta_{\text{f}} H^{\circ} [\text{CO}_{2}(g)] - [\Delta_{\text{f}} H^{\circ} [\text{C}_{60}(s)] + 60\Delta_{\text{f}} H^{\circ} [\text{O}_{2}(g)]] = -26367 \text{kJ/mole}$$

$$60(-393.51 \text{kJ/mol}) - x - 0 = -26367 \text{kJ/mole}$$

 $\Delta_f \text{H}^{\circ}[\text{C}_{60}(\text{s})] = 2757 \text{kJ/mole}$

2.80. The reactions are:

$$2\times[\text{NaHCO}_{3}(s) \rightarrow \text{Na}(s) + \frac{1}{2} \text{H}_{2}(g) + \text{C}(s) + \frac{3}{2} \text{O}_{2}(g)] \ 2 \times -\Delta_{f}H = +1901.62 \text{ kJ}$$

$$2 \text{ Na}(s) + \text{C}(s) + \frac{3}{2} \text{O}_{2}(g) \rightarrow \text{Na}_{2}\text{CO}_{3}(s)$$

$$\Delta_{f}H = -1130.77 \text{ kJ}$$

$$C(s) + \text{O}_{2}(g) \rightarrow \text{CO}_{2}(g)$$

$$\Delta_{f}H = -393.51 \text{ kJ}$$

$$H_{2}(g) + \frac{1}{2} \text{O}_{2}(g) \rightarrow \text{H}_{2}\text{O}(1)$$

$$\Delta_{f}H = -285.83 \text{ kJ}$$

This yields the overall reaction (you can verify that), and the overall $\Delta_{rxn}H$ is the sum of the values on the right: $\Delta_{rxn}H = 91.51$ kJ.

- **2.82.** The reaction is 2 Al (s) + Fe₂O₃ (s) \rightarrow Al₂O₃ (s) + 2 Fe (s). The $\Delta_{rxn}H$ is (using data from the appendix): (2 mol)(0 kJ/mol) + (1 mol)(-1675.7 kJ/mol) (1 mol)(-825.5 kJ/mol) (2 mol)(0 kJmol) = -850.2 kJ.
- **2.84.** In this case, since the combustion occurs in open atmosphere in (assumed) constant pressure, this time $q_p = \Delta H = -31,723$ J. If the expansion of gases is done against a constant atmospheric pressure of 1 atm, to determine work we need to know the net volume of gas produced. From exercise 2.55, we found that there was a net change of -0.00491 mol of gas produced (ignoring the volume of the benzoic acid itself). Thus,

$$V = \frac{nRT}{p} = \frac{(0.0049 \text{ mol})(0.08205 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(24.6 + 273.15)}{1 \text{ atm}} = 0.120 \text{ Lless gas volume}$$

Using this change in volume to calculate work:

$$w = -p_{ext}\Delta V = -(1 \text{ atm})(-0.120 \text{ L}) \times \frac{101.32 \text{ J}}{1 \text{ L} \cdot \text{atm}} = +12.1 \text{ J}$$

Finally, to calculate ΔU :

$$\Delta U = \Delta H + \Delta (pV) = \Delta H + (\Delta n)RT = -31,723 + (-0.00491 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(24.6 + 273.15)$$

$$\Delta U = -31,723 - 12.1 \text{ J} = -31,711 \text{ J}$$

2.86. This problem is very similar to Example 2.19, so we will follow that example, taking data from Table 2.1.

The heat needed to bring the reactants from 500°C (or 773 K) to 298 K is:

$$\Delta H_1 = q = (2 \text{ mol})(2.02 \text{ g/mol})(14.304 \text{ J/g·K})(-475 \text{ K}) + (1 \text{ mol})(32.00 \text{ g/mol})$$

(0.918 J/g·K)(-475 K) = -41403 J

The heat of reaction is $2\times(\Delta_f H[H_2O(g)]) = 2 \text{ mol} \times -241.8 \text{ kJ/mol} = -483.6 \text{ kJ} = \Delta H_2$

The heat needed to bring the products from 298 K to 500°C (or 773 K) is:

$$\Delta H_3 = q = (2 \text{ mol})(18.02 \text{ g/mol})(1.864 \text{ J/g} \cdot \text{K})(475 \text{ K}) = +31,910 \text{ J}$$

The overall $\Delta_{rxn}H$ is the sum of these three parts. Converting all energy values to kJ:

$$\Delta_{\text{rxn}}H = -41.403 \text{ kJ} - 483.6 \text{ kJ} + 31.910 \text{ kJ} = -493.1 \text{ kJ}$$