## SOLUTIONS MANUAL



## 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. $1780 \operatorname{torr}\left(\frac{1 \mathrm{~atm}}{760 \mathrm{torr}}\right)=2.34 \mathrm{~atm}$
$w=-P \Delta V=-2.34 \mathrm{~atm}(1.00 \mathrm{~L}-3.55 \mathrm{~L})\left(\frac{101.32 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}\right)=+605 \mathrm{~J}$
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 $\mathrm{CO}_{2}$. Using $\mathrm{P}_{1} \mathrm{~V}_{1}=\mathrm{P}_{2} \mathrm{~V}_{2}$, we find that $\mathrm{V}_{2}=105 \mathrm{~mL}$
$\mathrm{w}=-(1.0 \mathrm{~atm})(105-25.0 \mathrm{~mL})\left(\frac{1 \mathrm{~L}}{1000 \mathrm{~mL}}\right)\left(\frac{101.32 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}\right)=-8.1 \mathrm{~J}$
2.10. First, determine the $\Delta T: 330 \mathrm{~K}-298 \mathrm{~K}=32 \mathrm{~K}$.

Using $q=m \cdot c \cdot \Delta T$, we rearrange : $c=\frac{q}{m \cdot \Delta T}$
Substituting: $c=\frac{288 \mathrm{~J}}{(50.5 \mathrm{~g})(32 \mathrm{~K})}=0.178 \frac{\mathrm{~J}}{\mathrm{~g} \cdot \mathrm{~K}}$.
2.12. First, we need to calculate the number of moles of phosphorous:

$$
\begin{aligned}
& 50.0 \mathrm{~g} \mathrm{P}\left(\frac{1 \mathrm{~mole}}{30.97 \mathrm{~g}}\right)=1.61 \mathrm{moles} \mathrm{P} \\
& q=\int_{298}^{350}(1.61 \text { moles })\left(56.99+0.1202 \mathrm{~T} \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}}\right) d T \\
& q=\left.1.61 \mathrm{moles}\left[56.99 T+\frac{0.1202 \mathrm{~T}^{2}}{2}\right]\right|_{298} ^{350}=8.03 \times 10^{3} \mathrm{~J}
\end{aligned}
$$

2.14. The kinetic energy of the hailstone, KE , is equal to:
$\frac{1}{2} \mathrm{mv}^{2}=\frac{1}{2}\left(6.0 \times 10^{-5} \mathrm{~kg}\right)(10.0 \mathrm{~m} / \mathrm{s})^{2}=3.0 \times 10^{-3} \mathrm{~J}$
Since all of the kinetic energy is converted into thermal energy, we can say that:
$K E=m \cdot c \cdot \Delta T$
$3.0 \times 10^{-3} J=\left(6.0 \times 10^{-2} g\right)\left(2.06 \frac{J}{g \cdot K}\right)(\Delta T)$
$\Delta T=0.024 K$
2.16. First, calculate the energy needed to warm the water by $1.00^{\circ} \mathrm{C}$ :
$q=m \cdot c \cdot \Delta T=\left(1.00 \times 10^{5} \mathrm{~g}\right)(4.18 \mathrm{~J} / \mathrm{g} \cdot \mathrm{K})(1.00 \mathrm{~K})=4.18 \times 10^{5} \mathrm{~J}$
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
$m g h=(20.0 \mathrm{~kg})\left(9.81 \mathrm{~m} / \mathrm{s}^{2}\right)(2.00 \mathrm{~m})=392.4 \mathrm{~J}$. Therefore,
\# drops $=\frac{4.18 \times 10^{5} \mathrm{~J}}{392.4 \mathrm{~J} / \text { drop }}=1065$ 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. $q=-124.0 \mathrm{~J}$
$w=-p_{\text {ext }} \Delta V=-(1550$ torr $)(119 \mathrm{~mL}-377 \mathrm{~mL}) \times \frac{1 \mathrm{~atm}}{760 \mathrm{torr}} \times \frac{1 \mathrm{~L}}{1000 \mathrm{~mL}}=+0.526 \mathrm{~L} \cdot \mathrm{~atm}$ $w=+0.526 \mathrm{~L} \cdot \mathrm{~atm} \times \frac{101.32 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}=+53.3 \mathrm{~J}$
Since $\Delta U=q+w, \Delta U=-124.0 \mathrm{~J}+53.3 \mathrm{~J} \quad \Delta U=-70.7 \mathrm{~J}$
2.24. Reversibly: $w=-n R T \ln \frac{V_{f}}{V_{i}}=-(1 \mathrm{~mol})(8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K})(298.0 \mathrm{~K}) \ln \frac{10 \mathrm{~L}}{1.0 \mathrm{~L}}=-5705 \mathrm{~J}$ Irreversibly: $w=-p_{\text {ext }} \Delta V=-(1.00 \mathrm{~atm})(10 \mathrm{~L}-1.0 \mathrm{~L}) \times \frac{101.32 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}=-912 \mathrm{~J}$

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 $\Delta U$ 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:
$p V=n R T$ can be rearranged to $n=\frac{p V}{R T}=\frac{(172 \mathrm{~atm})(80.0 \mathrm{~L})}{\left(0.08205 \frac{\mathrm{~L} \cdot \mathrm{~atm}}{\mathrm{~mol} \cdot \mathrm{~K}}\right)(20.0+273.15 \mathrm{~K})}$
$n=572 \mathrm{~mol} \mathrm{~N}_{2}$ gas
(a) The final pressure can be determined using Charles' law: $\frac{p_{i}}{T_{i}}=\frac{p_{f}}{T_{f}}$

$$
p_{f}=\frac{p_{i} T_{f}}{T_{i}}=\frac{(172 \mathrm{~atm})(140.0+273.15 \mathrm{~K})}{(20.0+273.15 \mathrm{~K})} \quad p_{f}=242 \mathrm{~atm}
$$

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

$$
\begin{aligned}
& q=n \cdot \bar{C}_{V} \cdot \Delta T=(572 \mathrm{~mol})(21.0 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K})\left(140.0^{\circ} \mathrm{C}-20.0^{\circ} \mathrm{C}\right)=1.44 \times 10^{6} \mathrm{~J} \\
& \Delta U=q+w=1.44 \times 10^{6} \mathrm{~J}+0=1.44 \times 10^{6} \mathrm{~J} .
\end{aligned}
$$

2.34. $w=-n R T \ln \frac{V_{f}}{V_{i}}=-(0.505 \mathrm{~mol})\left(8.314 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}}\right)(5.0+273.15 \mathrm{~K}) \ln \frac{0.10 \mathrm{~L}}{1.0 \mathrm{~L}}=+2689 \mathrm{~J}$
$q=-2690 \mathrm{~J}$ (given)
$\Delta U=q+w=-2690 \mathrm{~J}+2689 \mathrm{~J}=-1 \mathrm{~J}$
$\Delta H=\Delta U+\Delta(p V)$ Since the process occurs at constant temperature, Boyle's law applies and $\Delta(p V)=0$. Therefore, $\Delta H=-1 \mathrm{~J}$.
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, $\Delta H=q_{\mathrm{p}}$ and $\Delta H=+2260 \mathrm{~J} / \mathrm{g}$.

For work, we need change in volume. Assuming the ideal gas law holds, the volume of 1 gram of steam at $100^{\circ} \mathrm{C}(373.15 \mathrm{~K})$ is:
$n=1 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} \times \frac{1 \mathrm{~mol}}{18.02 \mathrm{~g}}=0.0555 \mathrm{~mol}$
$V=\frac{n R T}{p}=\frac{(0.0555 \mathrm{~mol})(0.08205 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{K})(373.15 \mathrm{~K})}{0.988 \mathrm{~atm}}=1.720 \mathrm{~L}$
The volume of a gram of water, 1.00 mL , is negligible compared to this. Therefore, let us use $\Delta V=1.720 \mathrm{~L}$. Therefore:
$w=-(0.988 \mathrm{~atm})(1.720 \mathrm{~L}) \times \frac{101.32 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}=-172 \mathrm{~J}$
Since $\Delta U=q+w$, we have $\Delta U=+2260 \mathrm{~J}-172 \mathrm{~J}=2088 \mathrm{~J}$.
2.38. In terms of pressure and volume: $d U=\left(\frac{\partial U}{\partial p}\right)_{V} d p+\left(\frac{\partial U}{\partial V}\right)_{p} d V$.

For enthalpy: $d H=\left(\frac{\partial H}{\partial p}\right)_{V} d p+\left(\frac{\partial H}{\partial V}\right)_{p} d V$.
2.40. $\mathrm{w}=-\mathrm{P} \Delta \mathrm{V}=0$; There is no change in volume. Assuming the heat capacity of an ideal gas:
$\Delta U=q=\int_{348.45}^{29 \mathrm{~g}} 15 \bar{C}_{v} d T=\int_{348.45}^{298.15}(35.0 \mathrm{~g})\left(\frac{1 \mathrm{~mole}}{2.016 \mathrm{~g}}\right)\left(20.78 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}}\right) d T=\left.\left(361 \frac{\mathrm{~J}}{\mathrm{~K}}\right) T\right|_{348.45} ^{298.15}=-1.82 \times 10^{4} \mathrm{~J}$
Using the ideal gas law:

$$
\begin{aligned}
& \Delta H=\Delta U+\Delta(P V)=\Delta U+V \Delta P=\Delta U+V\left(\frac{n R \Delta T}{V}\right) \\
& =-1.82 \times 10^{4} J+(35.0 g)\left(\frac{1 \text { mole }}{2.016 g}\right)\left(8.314 \frac{J}{K \cdot m o l}\right)(298.15-348.45 \mathrm{~K})=-2.55 \times 10^{4} \mathrm{~J}
\end{aligned}
$$

2.42. $q=m \cdot s \cdot \Delta T=(244 g)\left(4.184 \frac{\mathrm{~J}}{\mathrm{~K} \cdot \mathrm{~mol}}\right)(20.0-80.0 \mathrm{~K})=-6.13 \times 10^{4} \mathrm{~J}$

Since it is a constant pressure process (assumed 1 atm ), $\Delta \mathrm{H}=-6.13 \times 10^{4} \mathrm{~J}$.
Now, we need to calculate the volume change of the coffee:
$\Delta V=\Delta\left(\frac{\text { mass }}{\text { density }}\right)=(244 \mathrm{~g})\left(\frac{1 \mathrm{~cm}^{3}}{0.9982 g}-\frac{1 \mathrm{~cm}^{3}}{0.9718 \mathrm{~g}}\right)=-6.64 \mathrm{~cm}^{3}$
$w=-P \Delta V=-(1 \mathrm{~atm})\left(-6.64 \mathrm{~cm}^{3}\right)\left(\frac{1 \mathrm{~mL}}{\mathrm{~cm}^{3}}\right)\left(\frac{1 L}{1000 \mathrm{~mL}}\right)\left(\frac{101.32 \mathrm{~J}}{1 L \cdot \mathrm{~atm}}\right)=0.673 \mathrm{~J}$
$\Delta U=q+w=-61300 J+0.67 J=-6.13 \times 10^{4} J$
2.44. Start with $\overline{\Delta U}=\bar{C}_{V} \Delta T$ and $\overline{\Delta H}=\overline{\Delta U}+\Delta(p \bar{V})$ : Since $p \bar{V}=R T$ for an ideal gas, we also have $\overline{\Delta H}=\overline{\Delta U}+\Delta(R T)$. Substituting for $\overline{\Delta H}$ (equation 2.32 ) and $\overline{\Delta U}$ (equation 2.27): $\bar{C}_{p} \Delta T=\bar{C}_{v} \Delta T+\Delta(R T)$

R is a constant, so it can be removed from the $\Delta$ term:
$\bar{C}_{p} \Delta T=\bar{C}_{v} \Delta T+R \Delta T$
Now all terms can be divided by $\Delta T$ to get the desired relationship:
$\bar{C}_{p}=\bar{C}_{v}+R$.
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 $\mu_{\mathrm{JT}}=\frac{\Delta T}{\Delta p}$ :
$\Delta \mathrm{p}=0.95 \mathrm{~atm}-200.00 \mathrm{~atm}=-199.05 \mathrm{~atm}$ Since $\mu_{\mathrm{JT}}=0.150 \mathrm{~K} / \mathrm{atm}:$

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

If the initial temperature is $19.0^{\circ} \mathrm{C}$ and the temperature drops by 29.9 degrees, the final temperature should be about $19.0-29.9=-10.9^{\circ} \mathrm{C}$.
2.52. $\mu_{\mathrm{JT}}$ for Argon at $0^{\circ} \mathrm{C}$ and 1 atm is $0.4307 \mathrm{~K} /$ atm. From Eqn 2.35 we know that: $\left(\frac{\partial H}{\partial P}\right)_{T}=-\bar{C}_{P} \cdot \mu_{J T}=-\left(20.8 \frac{\mathrm{~J}}{\mathrm{~K} \cdot \mathrm{~mol}}\right)\left(0.4307 \frac{\mathrm{~K}}{\mathrm{~atm}}\right)=-8.96 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~atm}} ; \bar{C}_{P}$ for a monatomic ideal gas is equal to $\frac{5}{2} R$.
2.54. Although $\Delta U$ and $\Delta H$ 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 $H$. In addition, the Joule-Thomson experiment is originally defined (as is $\mu_{\mathrm{JT}}$ ) for an isenthalpic process, not one for which $U$ is constant. Therefore, that definition of $\mu_{\mathrm{JT}}$ would probably not be proper.
2.56. Since $\bar{C}_{V}=\frac{3}{2} R$ and $\bar{C}_{p}=\frac{5}{2} R$ :
$\frac{3}{2} R=\frac{3}{2}(8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}) \times \frac{1 \mathrm{cal}}{4.184 \mathrm{~J}}=2.981 \mathrm{cal} / \mathrm{mol} \cdot \mathrm{K}$
Or, in different units: $\frac{3}{2}(0.08205 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{K})=0.1231 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{K}$
$\frac{5}{2} R=\frac{5}{2}(8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}) \times \frac{1 \mathrm{cal}}{4.184 \mathrm{~J}}=4.968 \mathrm{cal} / \mathrm{mol} \cdot \mathrm{K}$
Or, in different units: $\frac{5}{2}(0.08205 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{K})=0.2051 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{K}$
2.58. $\bar{C}_{V}$ for a monatomic ideal gas is equal to $\frac{3}{2} R$. Using the equation $\Delta U=w=n \bar{C}_{V} \Delta T:-75$ $\mathrm{J}=(0.122 \mathrm{~mol})(12.47 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}) \cdot \Delta T$ and solve for $\Delta T$ :
$\Delta T=-49 \mathrm{~K}$. Since the initial temperature was $235^{\circ} \mathrm{C}=508 \mathrm{~K}$, the final temperature is 508 $-49=459 \mathrm{~K}$.
2.60. $\gamma=\frac{\overline{\mathrm{C}}_{\mathrm{P}}}{\overline{\mathrm{C}}_{\mathrm{V}}}$. For a monatomic ideal gas, $\gamma=\frac{\left(\frac{5 \mathrm{R}}{2}\right)}{\left(\frac{3 \mathrm{R}}{2}\right)}=\frac{5}{3}$
2.62. (a) $\mathrm{CO}_{2}$ is a linear polyatomic molecule where $\mathrm{N}=3$ atoms. In the low temperature limit it only has contributions from translational and rotational motion so
$\overline{\mathrm{C}}_{\mathrm{V}}=\frac{3}{2} \mathrm{R}+\mathrm{R}=\frac{5}{2} \mathrm{R} \cdot \overline{\mathrm{C}}_{\mathrm{P}}=\frac{7}{2} \mathrm{R}$, so $\gamma=\frac{\overline{\mathrm{C}}_{\mathrm{P}}}{\overline{\mathrm{C}}_{\mathrm{V}}}=\frac{7}{5}$. In the high temperature limit,
vibrational motion contributes as well so:
$\overline{\mathrm{C}}_{\mathrm{V}}=\frac{5}{2} \mathrm{R}+(3 \mathrm{~N}-5) \mathrm{R}=\frac{13}{2} \mathrm{R} . \overline{\mathrm{C}}_{\mathrm{P}}=\frac{15}{2} \mathrm{R}$, so $\gamma=\frac{\overline{\mathrm{C}}_{\mathrm{P}}}{\overline{\mathrm{C}}_{\mathrm{V}}}=\frac{15}{13}$
(b) $\mathrm{H}_{2} \mathrm{O}$ is a non-linear polyatomic molecule where $\mathrm{N}=3$ atoms. In the low temperature limit it only has contributions from translational and rotational motion so
$\overline{\mathrm{C}}_{\mathrm{V}}=\frac{3}{2} \mathrm{R}+\frac{3}{2} \mathrm{R}=3 \mathrm{R} . \overline{\mathrm{C}}_{\mathrm{P}}=4 \mathrm{R}$, so $\gamma=\frac{\overline{\mathrm{C}}_{\mathrm{p}}}{\overline{\mathrm{C}}_{\mathrm{V}}}=\frac{4}{3}$. In the high temperature limit,
vibrational motion contributes as well so:

$$
\overline{\mathrm{C}}_{\mathrm{V}}=3 \mathrm{R}+(3 \mathrm{~N}-6) \mathrm{R}=6 \mathrm{R} \cdot \overline{\mathrm{C}}_{\mathrm{P}}=7 \mathrm{R} \text {, so } \gamma=\frac{\overline{\mathrm{C}}_{\mathrm{P}}}{\overline{\mathrm{C}}_{\mathrm{V}}}=\frac{7}{6}
$$

2.64. Using Eqn. 2.47: $\left(\frac{\mathrm{V}_{\mathrm{i}}}{\mathrm{V}_{\mathrm{f}}}\right)^{2 / 3}=\frac{\mathrm{T}_{\mathrm{f}}}{\mathrm{T}_{\mathrm{i}}}$
$\left(\frac{V_{i}}{2 V_{i}}\right)^{2 / 3}=\frac{x}{T_{i}} ; \quad x=0.63 T_{i} ; \quad$ The final temperature is $63 \%$ of the initial temperature.
2.66. For an adiabatic change, $\left(\frac{p_{f}}{p_{i}}\right)^{2 / 5}=\frac{T_{f}}{T_{i}}$. Therefore, $\left(\frac{p_{f}}{p_{i}}\right)^{2 / 5}=\left(\frac{0.00074 \mathrm{~atm}}{0.0033 \mathrm{~atm}}\right)^{2 / 5}=0.550$.

Therefore, the absolute temperature will drop to $55 \%$ of its initial temperature.
2.68. As vibrational energies begin to have more significance, $\gamma$ decreases. As $\gamma$ 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) $\mathrm{N}_{2}$ and CO have nearly identical molar masses, M . What is different between the two gases is $\gamma$ 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:

$$
\text { speed }=\sqrt{\frac{\left(\frac{7}{5}\right)\left(8.314 \frac{\mathrm{~J}}{\mathrm{~K} \cdot \mathrm{~mol}}\right)(100 \mathrm{~K})}{0.04401 \frac{\mathrm{~kg}}{\mathrm{~mol}}}}=163 \mathrm{~m} / \mathrm{s}
$$

At 500 K :

$$
\text { speed }=\sqrt{\frac{\left(\frac{15}{13}\right)\left(8.314 \frac{\mathrm{~J}}{\mathrm{~K} \cdot \mathrm{~mol}}\right)(500 \mathrm{~K})}{0.04401 \frac{\mathrm{~kg}}{\mathrm{~mol}}}}=330 \mathrm{~m} / \mathrm{s}
$$

2.72. The volumes of both water and ice at $0^{\circ} \mathrm{C}$ are:
water: $V_{1}=\frac{18.02 \mathrm{~g}}{0.99984 \mathrm{~g} / \mathrm{mL}}=18.02 \mathrm{~mL}$; ice: $V_{\mathrm{s}}=\frac{18.02 \mathrm{~g}}{0.9168 \mathrm{~g} / \mathrm{mL}}=19.66 \mathrm{~mL}$.
Therefore, $\Delta V=19.66 \mathrm{~mL}-18.92 \mathrm{~mL}=0.74 \mathrm{~mL}$, so that the work is $w=-p_{\text {ext }} \Delta V=-(1$ bar $)\left(\frac{1 \mathrm{~atm}}{1.01325 \mathrm{bar}}\right) \times(0.74 \mathrm{~mL})\left(\frac{1 L}{1000 \mathrm{~mL}}\right)\left(\frac{101.32 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}\right)=-0.074 \mathrm{~J}$.
2.74. According to Table 2.3, 1 gram of $\mathrm{H}_{2} \mathrm{O}$ gives up 2260 J when it condenses. Since each gram of ice requires 333.5 J to melt, we get
$2260 \mathrm{~J} \times \frac{1 \mathrm{~g}}{333.5 \mathrm{~J}}=6.78$ grams of ice that can be melted.
2.76. $\Delta_{r x n} H=\sum \Delta_{f} H($ prods $)-\sum \Delta_{f} H($ rcts $)=(2 \mathrm{~mol})(26.5 \mathrm{~kJ} / \mathrm{mol})-0-0=53.0 \mathrm{~kJ}$
2.78. $\Delta_{\text {rxn }} \mathrm{H}=60 \Delta_{\mathrm{f}} \mathrm{H}^{0}\left[\mathrm{CO}_{2}(\mathrm{~g})\right]-\left[\Delta_{\mathrm{f}} \mathrm{H}^{\circ}\left[\mathrm{C}_{60}(\mathrm{~s})\right]+60 \Delta_{\mathrm{f}} \mathrm{H}^{\circ}\left[\mathrm{O}_{2}(\mathrm{~g})\right]\right]=-26367 \mathrm{~kJ} / \mathrm{mole}$ $60(-393.51 \mathrm{~kJ} / \mathrm{mol})-\mathrm{x}-0=-26367 \mathrm{~kJ} / \mathrm{mole}$
$\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}\left[\mathrm{C}_{60}(\mathrm{~s})\right]=2757 \mathrm{~kJ} / \mathrm{mole}$
2.80. The reactions are:

$$
\begin{array}{cc}
2 \times\left[\mathrm{NaHCO}_{3}(\mathrm{~s}) \rightarrow \mathrm{Na}(\mathrm{~s})+1 / 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{C}(\mathrm{~s})+3 / 2 \mathrm{O}_{2}(\mathrm{~g})\right] 2 \times-\Delta_{\mathrm{f}} H=+1901.62 \mathrm{~kJ} \\
2 \mathrm{Na}(\mathrm{~s})+\mathrm{C}(\mathrm{~s})+3 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{~s}) & \Delta_{\mathrm{f}} H=-1130.77 \mathrm{~kJ} \\
\mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) & \Delta_{\mathrm{f}} H=-393.51 \mathrm{~kJ} \\
\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) & \Delta_{\mathrm{f}} H=-285.83 \mathrm{~kJ}
\end{array}
$$

This yields the overall reaction (you can verify that), and the overall $\Delta_{\mathrm{rxn}} H$ is the sum of the values on the right: $\Delta_{\mathrm{rxn}} H=91.51 \mathrm{~kJ}$.
2.82. The reaction is $2 \mathrm{Al}(\mathrm{s})+\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s}) \rightarrow \mathrm{Al}_{2} \mathrm{O}_{3}(\mathrm{~s})+2 \mathrm{Fe}(\mathrm{s})$. The $\Delta_{\mathrm{rxn}} H$ is (using data from the appendix $):(2 \mathrm{~mol})(0 \mathrm{~kJ} / \mathrm{mol})+(1 \mathrm{~mol})(-1675.7 \mathrm{~kJ} / \mathrm{mol})-(1 \mathrm{~mol})(-825.5 \mathrm{~kJ} / \mathrm{mol})-(2$ $\mathrm{mol})(0 \mathrm{kJmol})=-850.2 \mathrm{~kJ}$.
2.84. In this case, since the combustion occurs in open atmosphere in (assumed) constant pressure, this time $q_{\mathrm{p}}=\Delta H=-31,723 \mathrm{~J}$. 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, $V=\frac{n R T}{p}=\frac{(0.0049 \mathrm{~mol})(0.08205 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{K})(24.6+273.15)}{1 \mathrm{~atm}}=0.120 \mathrm{~L}$ less gas volume

Using this change in volume to calculate work:
$w=-p_{\text {ext }} \Delta V=-(1 \mathrm{~atm})(-0.120 \mathrm{~L}) \times \frac{101.32 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}=+12.1 \mathrm{~J}$
Finally, to calculate $\Delta U$ :
$\Delta U=\Delta H+\Delta(p V)=\Delta H+(\Delta n) R T=-31,723+(-0.00491 \mathrm{~mol})(8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K})(24.6+273.15)$
$\Delta U=-31,723-12.1 \mathrm{~J}=-31,711 \mathrm{~J}$
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 $500^{\circ} \mathrm{C}$ (or 773 K ) to 298 K is:
$\Delta H_{1}=q=(2 \mathrm{~mol})(2.02 \mathrm{~g} / \mathrm{mol})(14.304 \mathrm{~J} / \mathrm{g} \cdot \mathrm{K})(-475 \mathrm{~K})+(1 \mathrm{~mol})(32.00 \mathrm{~g} / \mathrm{mol})$ $(0.918 \mathrm{~J} / \mathrm{g} \cdot \mathrm{K})(-475 \mathrm{~K})=-41403 \mathrm{~J}$

The heat of reaction is $2 \times\left(\Delta_{\mathrm{f}} H\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{g})\right]\right)=2 \mathrm{~mol} \times-241.8 \mathrm{~kJ} / \mathrm{mol}=-483.6 \mathrm{~kJ}=\Delta H_{2}$ The heat needed to bring the products from 298 K to $500^{\circ} \mathrm{C}$ (or 773 K ) is:
$\Delta H_{3}=q=(2 \mathrm{~mol})(18.02 \mathrm{~g} / \mathrm{mol})(1.864 \mathrm{~J} / \mathrm{g} \cdot \mathrm{K})(475 \mathrm{~K})=+31,910 \mathrm{~J}$
The overall $\Delta_{\mathrm{rxn}} H$ is the sum of these three parts. Converting all energy values to kJ :

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

