

$$1. \quad P = 1 \text{ atm} \quad n = 1 \text{ mol} \quad R = 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad T = 100^\circ\text{C} + 273 = 373 \text{ K}$$

$$w = -P\Delta V = -P \times \frac{nRT}{P} = -nRT$$

$$w = -1 \times 8.3145 \times 373 = -3101.3085 \text{ J}$$

$$2. \quad \Delta U = q + w \quad q = 0 \text{ (evaporation from the surface of liquid)}$$

$$\Rightarrow \Delta U = w = -3101.3085 \text{ J}$$

$$\Delta H = \Delta U + P\Delta V = \Delta U + \frac{P \times nRT}{P} = \Delta U + nRT$$

$$\Rightarrow \Delta H = -3101.3085 + 1 \times 8.3145 \times 373 = 0$$

$$3. \quad \text{adiabatic} \Rightarrow q = 0 \quad \Delta U = w + q \uparrow^0 \quad \Delta U = C_v \Delta T$$

$$\Rightarrow C_v \Delta T = w \quad \Rightarrow C_v dT = -nRT \frac{dV}{V} \quad \Rightarrow \int C_v \frac{dT}{T} = -nR \int \frac{dV}{V}$$

$$\Rightarrow C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \quad , \quad C_v = \frac{3R}{2} \quad V_2 = 44.8 \text{ L}$$

$$\Rightarrow \frac{3}{2} R \ln \frac{T_2}{T_1} = -1 \times R \ln \frac{22.4}{44.8}$$

$$V_1 = 22.4 \text{ L}$$

$$T_1 = 0^\circ\text{C} + 273$$

$$\Rightarrow \ln \frac{T_2}{T_1} = -\frac{2}{3} \times -0.69315 = 0.4621$$

$$\Rightarrow \frac{T_2}{T_1} = 1.587 \quad \Rightarrow T_2 = 1.587 \times 273 = 433.36 \text{ K}$$

4-

(a) Assume ammonia is an ideal gas. The final temperature is

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(1.00 \text{ atm})(23.5 \text{ L})}{(1.00 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})} = 286 \text{ K}$$

(b) The problem provides enough information to calculate w and ΔU directly. Consequently, q can be determined using the first law of thermodynamics.

w is related to the change in volume of the system. The final volume is given, but the initial volume needs to be calculated from the ideal gas law:

$$V_1 = \frac{nRT_1}{P_1} = \frac{(1.00 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{14.0 \text{ atm}} = 1.75 \text{ L}$$

The work done is

$$w = -P_{\text{ex}} \Delta V = -(1.00 \text{ atm})(23.5 \text{ L} - 1.75 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -2.20 \times 10^3 \text{ J}$$

ΔU is related to C_V , which can be calculated from $\bar{C}_p = 35.66 \text{ J K}^{-1} \text{ mol}^{-1}$ listed in Appendix 2. It is assumed that C_V and C_p are independent of temperature.

$$\begin{aligned} C_V &= C_p - nR \\ &= (1.00 \text{ mol}) (35.66 \text{ J K}^{-1} \text{ mol}^{-1}) - (1.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 27.35 \text{ J K}^{-1} \end{aligned}$$

The change in internal energy is

$$\Delta U = C_V \Delta T = (27.35 \text{ J K}^{-1}) (286 \text{ K} - 298 \text{ K}) = -3.3 \times 10^2 \text{ J}$$

Using the first law of thermodynamics,

$$q = \Delta U - w = -3.3 \times 10^2 \text{ J} - (-2.20 \times 10^3 \text{ J}) = 1.87 \times 10^3 \text{ J}$$

5-

The thermal energy supplied as heat is used to overcome the attractive, intermolecular forces between the acetone molecules. The molecules then break free of the condensed, liquid phase and enter the gas phase. Since the added energy is converted to potential and not kinetic energy of the molecules, the temperature remains constant.

6-

$$\begin{aligned}\Delta_r H^\circ &= 2\Delta_f \bar{H}^\circ [\text{C}_2\text{H}_5\text{OH}(l)] + 2\Delta_f \bar{H}^\circ [\text{CO}_2(g)] - \Delta_f \bar{H}^\circ [\text{C}_6\text{H}_{12}\text{O}_6(s)] \\ &= 2(-277.0 \text{ kJ mol}^{-1}) + 2(-393.5 \text{ kJ mol}^{-1}) - (-1274.5 \text{ kJ mol}^{-1}) \\ &= -66.5 \text{ kJ mol}^{-1}\end{aligned}$$

7-

From the relationship

$$q = C_p \Delta T = n \bar{C}_p \Delta T$$

\bar{C}_p of benzene can be determined:

$$\bar{C}_p = \frac{q}{n \Delta T} = \frac{330 \text{ J}}{\left(\frac{24.6 \text{ g}}{78.11 \text{ g mol}^{-1}}\right) (28.7^\circ \text{C} - 21.0^\circ \text{C})} = 136 \text{ J mol}^{-1} \text{ }^\circ \text{C}^{-1}$$

8-

Since \bar{C}_p is temperature dependent, it has to be integrated over T to yield ΔH :

$$\begin{aligned}\Delta H &= \int_{298 \text{ K}}^{398 \text{ K}} n \bar{C}_p dT \\ &= \int_{298 \text{ K}}^{398 \text{ K}} (1 \text{ mol}) \left[(27.0 + 5.90 \times 10^{-3} T - 0.34 \times 10^{-6} T^2) \text{ J K}^{-1} \text{ mol}^{-1} \right] dT \\ &= \left[27.0T + 5.90 \times 10^{-3} \frac{T^2}{2} - 0.34 \times 10^{-6} \frac{T^3}{3} \right]_{298 \text{ K}}^{398 \text{ K}} \text{ J} \\ &= \left[27.0(398) + 5.90 \times 10^{-3} \frac{398^2}{2} - 0.34 \times 10^{-6} \frac{398^3}{3} \right] \text{ J} \\ &\quad - \left[27.0(298) + 5.90 \times 10^{-3} \frac{298^2}{2} - 0.34 \times 10^{-6} \frac{298^3}{3} \right] \text{ J} \\ &= 2.90 \times 10^3 \text{ J}\end{aligned}$$

9-

When an ideal gas undergoes an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -nRT \ln \frac{P_1}{P_2} = - (2 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) \ln \frac{1.00 \text{ atm}}{200 \text{ atm}} = 2.63 \times 10^4 \text{ J}$$

$$q = \Delta U - w = -w = -2.63 \times 10^4 \text{ J}$$

10-

The sublimation process can be considered a sum of the following processes:



Thus,

$$\Delta_{\text{sub}}H^\circ = 6.01 \text{ kJ mol}^{-1} + 44.01 \text{ kJ mol}^{-1} = 50.02 \text{ kJ mol}^{-1}$$

This value is an approximation, since the value of $\Delta_{\text{vap}}H^\circ$ is given at 298 K, whereas ice would not typically be found above 273 K.

Bonus:

Calculation of the enthalpy of combustion using bond enthalpies:

Type of bonds broken	Number of bonds broken	Bond enthalpy / $\text{kJ}\cdot\text{mol}^{-1}$	Enthalpy change / $\text{kJ}\cdot\text{mol}^{-1}$
C—H	12	414	4968
C—C	2	347	694
O=O	7	498.8	3491.6

Type of bonds broken	Number of bonds broken	Bond enthalpy / $\text{kJ}\cdot\text{mol}^{-1}$	Enthalpy change / $\text{kJ}\cdot\text{mol}^{-1}$
C=O	8	799	6392
O—H	12	460	5520

$$\Delta_r H^\circ = (4968 + 694 + 3491.6) \text{ kJ mol}^{-1} - (6392 + 5520) \text{ kJ mol}^{-1} = -2758 \text{ kJ mol}^{-1}$$

Calculation of the enthalpy of combustion using enthalpies of formation:

$$\begin{aligned}\Delta_r H^\circ &= 4\Delta_f \bar{H}^\circ [\text{CO}_2(\text{g})] + 6\Delta_f \bar{H}^\circ [\text{H}_2\text{O}(\text{l})] - 2\Delta_f \bar{H}^\circ [\text{C}_2\text{H}_6(\text{g})] - 7\Delta_f \bar{H}^\circ [\text{O}_2(\text{g})] \\ &= 4(-393.5 \text{ kJ mol}^{-1}) + 6(-285.8 \text{ kJ mol}^{-1}) - 2(-84.7 \text{ kJ mol}^{-1}) - 7(0 \text{ kJ mol}^{-1}) \\ &= -3119.4 \text{ kJ mol}^{-1}\end{aligned}$$

The value of $\Delta_r H^\circ$ so calculated is 13% greater than that calculated using bond enthalpies. The value determined using enthalpies of formation is the correct value, since it relies on the first law of thermodynamics. Bond enthalpies are averages determined for similar bonds in many molecules and provide estimates that are typically within 10% of the experimental value for any given, particular reaction.