

First Law of Thermodynamics

Answers and Explanations

1. D

Internal energy is a function of the state of the system. The difference in internal energy between two states is independent of the path taken between them.

2. A

Internal energy change results from the combination of heat flow and work between the system and its surroundings. Conservation of energy determines that the change in internal energy must equal the energy transferred between the system and its surroundings in terms of heat flow and thermodynamic work (pressure-volume work).

$$\begin{aligned} \Delta U &= Q - W \\ &= Q - P^* \Delta V \end{aligned}$$

ΔU = internal energy change
 Q = heat flow
 W = macroscopic work
 P^* = constant pressure
 ΔV = volume change

Internal energy is a function of the state of the system. We were told that the temperature increased somewhat between the initial and final state. For an ideal gas, internal energy depends on the temperature, so we know that internal energy increased.

$$U = \frac{3}{2}nRT$$

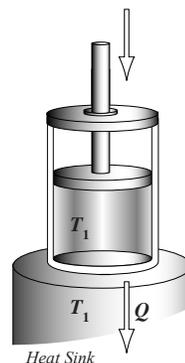
In summary, the internal energy increase is the same for all three paths shown. However, the combination of heat flow and thermodynamic work will be different for each path. On the pressure-volume curve, as the system moves to a greater volume, the work the system performs on the surroundings equals the area under the curve. It is easy to see that the system performed more work along path A. The expansion took place at higher pressures overall so the summation of work performed is greater as reflected in the greater area under the curve. Performing work on the surroundings *costs* the system energy, so if the system performed more work than the other paths but ended up with the same increased final internal energy, then more heat flow, Q , had to occur into the system during the expansion along path A than the other two, and, likewise, more heat flow into the system along path B than C.

3. B

An isothermal process takes place at constant temperature. For an ideal gas, internal energy exists only in the form of the kinetic energy of the particles, so if the temperature does not change for an ideal gas, the internal energy is constant.

$$U = \frac{3}{2}nRT$$

In an isothermal compression, energy added to the system due to work (pressure-volume work) simultaneously departs from the system as heat flow. Likewise, in an isothermal expansion, energy expended by the system in work is constantly replenished by heat flow into the system.



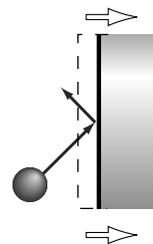
$$\begin{aligned} \Delta U &= 0 \\ Q &= -W \end{aligned}$$

First law of thermodynamics for an isothermal process

ΔU = internal energy change
 Q = heat flow
 W = macroscopic work

4. C

A molecule colliding with the piston head is colliding with a surface moving away from it. This means that while the collision occurs the molecule exerts a force over a distance, performing work ($W = (F \cos \theta)s$). The molecule performs work on the piston head and loses kinetic energy ($W = K_f - K_i \equiv \Delta K$) and thus speed.



5. C

An isothermal transformation is one with constant temperature. If the temperature is constant the pressure-volume product is constant.

$$PV = nRT$$

$$PV = \text{constant}$$

If the temperature is constant the pressure-volume product is constant. All three of the graphs correspond to a constant pressure-volume product except for C which shows volume decreasing exponentially with increased pressure.

6. B

The first law of thermodynamics tells us that if the internal energy of a system changes, there has to be exchange of energy with the surroundings. Some combination of heat flow and thermodynamic work (pressure-volume) work occurred.

$$\Delta U = Q - W$$

In this question our starting point is the heat flow into the system, the heat of vaporization accompanying the transformation of liquid water into water vapor, which we're asked to relate to the internal energy change. We can rearrange the 1st law to focus on the heat flow, Q .

$$Q = \Delta U + W$$

As heat flows into the liquid water and it transforms into water vapor, water molecules separate from one another along lines intermolecular force increasing in electrostatic potential energy. The water molecules have escaped from the potential energy wells into which they had fallen in the liquid state. Internal energy has increased.

But does the amount of internal energy increase equal the heat flow? That depends on whether or not the system's volume changed and thermodynamic work was performed. If a mole of water transformed into water vapor at 373K, the volume of the system expanded from .018L (the volume of 18g H₂O) to approximately 30L (the volume of a mole of gas at 100°C). The system had to perform work = $P\Delta V$ to push the atmosphere back!

In other words, more heat had to flow into the system than simply to bring about the internal energy increase

because energy was also required in the work of expanding against the surroundings.

$$Q^+ = \Delta U^+ + W^+$$

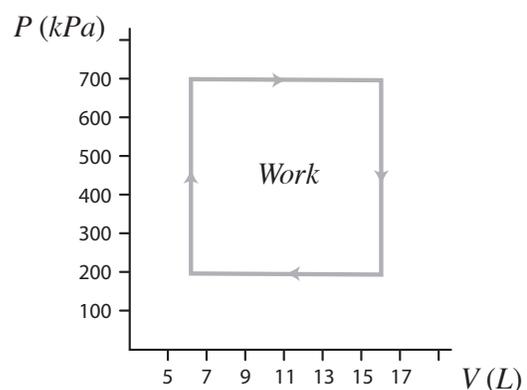
7. D

The question stem uses a bit of thermodynamics nomenclature you should be familiar with. An 'isochoric' transformation is constant volume. An 'isobaric' transformation is constant pressure.

We know that internal energy has no change over the entire cycle because the system returns to its initial state. If the internal energy change is zero, then the exchanges with the surroundings in terms of heat flow must be balanced by thermodynamic work. The engine took heat in, Q_{in} , during the isochoric heating and isobaric expansion stages and expelled heat, Q_{out} , during the isochoric cooling and isobaric compression stages. In order for $\Delta U = 0$, the difference between the heat taken in by this engine and the heat that the engine expels each cycle must equal the work performed.

$$W = Q_{in} - Q_{out}$$

The work performed each cycle equals the area enclosed by the pressure-volume curve.



$$W = (500 \text{ kPa})(10 \text{ L})$$

$$W = (5 \times 10^5 \text{ Pa})(1 \times 10^{-2} \text{ m}^3)$$

$$W = 5000 \text{ J}$$

$$Q_{in} - Q_{out} = 5000 \text{ J}$$

8. A

An isovolumetric process, also called isochoric, is a thermodynamic process during which the volume of the system remains constant. Because the volume is constant, no pressure-volume work is performed. In terms of the first law of thermodynamics, this means that the internal energy change will exactly equal the heat flow.

$$\Delta U = Q - W \quad \text{First law of thermodynamics}$$

$$W = 0 \quad \text{Isovolumetric - no work is performed}$$

$$\Delta U = Q \quad \text{First law for an isovolumetric process}$$

In chemistry, we almost always describe heat flow, Q , in terms of enthalpy change, ΔH . H is a state function whose change, ΔH , equals Q as long as pressure is constant. So why it is that the heat flow and internal energy change are so often equal in biochemistry?

Heat flow and internal energy change are often equal with biochemical reactions because the reagents and products are usually dissolved. The volume of the chemical system doesn't change with the reaction. Chemical reactions where the work function is significant are typically those with gaseous reagents or products, not dissolved solutes.

One of the most important kinds of intuition for chemistry is moving from the sense of the internal energy change in a reaction to the sense of whether the reaction is exothermic or endothermic and thus likely to be spontaneous or not. Most of the time in biochemistry this conceptual movement isn't going to be complicated by the work function. That's a good thing. If heat flow is happening you know it's because the internal energy changed and vice versa.

9. A

An adiabatic process occurs without any heat flow entering or leaving the system. If there is no heat flow, then any work performed on or by the system must directly correspond to internal energy change.

$$\Delta U = Q - W \quad \text{First law of thermodynamics}$$

$$Q = 0 \quad \text{'Adiabatic' means no heat flow}$$

$$\Delta U = -W \quad \text{The First law for an adiabatic process}$$

In other words, the helium in the piston increased in temperature because the surroundings performed work on the gas in the compression, and because the compression was adiabatic all of the energy input remains in the system. No heat flow occurred.

We could use calculus to integrate $P\Delta V$ through the incremental changes in pressure and volume to compute the work. That would be crazy! We have a much easier way to determine how much energy was added to the system. We could imagine a situation where the increase in internal energy *had* occurred by heat flow. It's not too hard to figure out how much heat flow is required to raise the temperature of 1.1L of helium at standard pressure by 40K ($\Delta T = 313\text{K} - 273\text{K} = 40\text{K}$)? The question stem helpfully tells us that the molar heat capacity of helium is $12.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$Q = n C \Delta T$$

$$\begin{aligned} Q &= \text{heat flow} \\ n &= \text{number of moles} \\ C &= \text{molar heat capacity} \\ \Delta T &= \text{temperature change} \end{aligned}$$

One mole of an ideal gas at STP occupies 22.4 L. How many moles are 1.1 L of helium at STP?

$$\left(\frac{\text{mol}}{22.4 \text{ L}} \right) (1.1 \text{ L}) = 0.05 \text{ mol}$$

How much heat flow would be required to raise this much helium gas by 40K?

$$\begin{aligned} Q &= (0.05 \text{ mol}) \left(12.5 \frac{\text{J}}{\text{mol K}} \right) (40 \text{ K}) \\ &= 25 \text{ J} \end{aligned}$$

That's the answer. Whether the internal energy increase occurred by means of heat flow into the system or by thermodynamic work, we can determine how much of an increase occurred through the change in temperature.

10. A

The 1st law tells us that if the internal energy of a system changes, there has to be exchange of energy with the surroundings. Some combination of heat flow and thermodynamic work (pressure-volume) work occurs.

$$\Delta U = Q - W$$

Let's rearrange this to focus on the heat flow, Q .

$$Q = \Delta U + W$$

The internal energy of the system decreases in the reaction. Oxygen is gaining electrons after all. However, the volume of the system also decreases. We're going from 3 moles of gas at STP to 2 moles of gas at STP, so the system loses 22.4 L of volume. What this means is that some of the heat flow from the system derives from the internal energy decrease and some of the heat flow from the system is due to the work being done on the system.

$$\bar{Q} = \bar{\Delta U} + \bar{W}$$

However, when the reaction is carried out at constant volume, there is no thermodynamic work. In that case the heat flow due to the compression won't be present. Only heat flow due to the original internal energy decrease occurs. At this stage we know enough to choose 'A' because that's the only choice having the reaction occurring in the bomb calorimeter as *less* exothermic.

If we want to be sure, we can determine the missing work. Before determining the thermodynamic work in the compression, remember to convert to SI units.

$$W = P\Delta V$$

$$\begin{aligned} W &= (2.2 \times 10^{-2} \text{ m}^3)(1 \times 10^5 \text{ Pa}) = 2.2 \times 10^3 \text{ J} \\ &= 2.2 \text{ kJ} \end{aligned}$$

11. D

The intake stroke is the isobaric expansion from state 5 to state 1. The exhaust stroke is the isobaric compression from state 1 to state 5. The work performed by the system (the area under the curve) for the intake stroke is exactly equal and opposite to the work performed on the system in the exhaust stroke.

12. B

This question is about whether you kept your footing in the passage enough to use one of the given formulas. The thermal efficiency is the percentage of the thermal energy produced in the combustion reaction that can be transformed into useful work. The passage presents the thermal efficiency as a function of compression ratio and heat capacity ratio.

$$\eta_{\text{th}} = 1 - \frac{1}{r^{\lambda-1}}$$

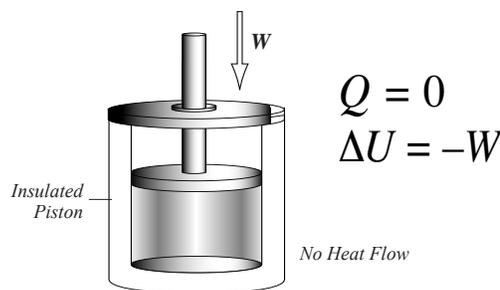
$$\eta_{\text{th}} = 1 - \frac{1}{8^{(1.33-1)}}$$

$$\eta_{\text{th}} = 1 - \frac{1}{8^{\frac{1}{3}}}$$

$$\eta_{\text{th}} = 1 - \frac{1}{2} = 50\%$$

13. A

The passage describes the compression stroke from state 1 to state 2 on the Otto cycle diagram as an adiabatic compression. No heat flows in an adiabatic compression, yet temperature increases due to the work performed on the system.



14. D

The 1st law tells us that if the internal energy of a system changes, there has to be exchange of energy with the surroundings. Some combination of heat flow and thermodynamic work (pressure-volume) work occurs.

$$\Delta U = Q - W$$

Let's rearrange this to focus on the heat flow, Q .

$$Q = \Delta U + W$$

In the combustion reaction, internal energy decreases through oxidation-reduction. However, the volume increases as the reaction is carried out at standard conditions (constant P of 1 atm) because the moles of CO_2 and H_2O gas produced are always greater than the moles of O_2 gas consumed. Because the system expands, the heat flow evolved will be less by the work performed than the internal energy decrease.

$$\bar{Q} = \Delta\bar{U} + \bar{W}$$

In the Otto cycle, though, combustion occurs isochorically (constant volume), the transformation from state 2 to state 3 on the diagram. Because no energy is lost to the work of expanding the system, the thermal energy introduced into the piston will be greater per mole of fuel than the heat of combustion of the fuel.

$$\bar{Q} = \Delta\bar{U}$$

When the volume doesn't change, the internal energy change exactly equals the heat flow.

15. B

This is a reading comprehension/association question. It depends on recognition that combustion produces the change from state 2 and state 3 on the Otto diagram. It also helps to understand that the product of a heat capacity and a temperature change is an increase in thermal energy.

16. C

As discussed in the passage, the compression ratio $r = V_1/V_2$, is the ratio of the volume of the piston at state 1 after expansion to the volume at state 2 after compression.

Choice **I** is correct. A higher compression ratio leads to greater efficiency as shown the following formula given in the passage (Note that as described in the passage λ must be a number greater than 1).

$$\eta_{\text{th}} = 1 - \frac{1}{(V_1/V_2)^{\lambda-1}} = 1 - \frac{1}{r^{\lambda-1}}$$

Choice **II** is also correct. A high compression ratio is consistent with a low volume at state 2 after adiabatic

compression. No heat flows in an adiabatic compression. The temperature increases due to the work performed on the system. Compression to a lower volume entails more work performed on the piston and a greater temperature of the fuel vapors prior to ignition. If the temperature after compression exceeds the autoignition temperature of the fuel vapors they will ignite without the need for a spark. This is exactly what happens in a diesel engine which has no spark plugs. Diesel engines are engineered with a higher compression ratio than gasoline engines.

Choice **III** is incorrect. Lower fuel vapor density prior to sparking is consistent with a higher volume at state 2. All else equal, a higher volume at state 2 would produce a lower compression ratio not a higher compression ratio.

