

## Heat Capacity

1. What is molar heat capacity?

The energy required to raise the temperature of 1 mol of a substance by 1K. Represented by, C.

2. What is specific heat capacity?

The energy required to raise the temperature of 1 gram of a substance by 1K. Represented by, C.

3. The kinetic energy of a system is directly related to its temperature. So if we heat a system we **increase** its kinetic energy.

4. What are two conditions under which a gas can be heated?

- a. **Constant Volume.** Under these circumstances no work can be performed. All the energy put into the system is in the form of heat energy.
- b. **Constant Pressure.** Under these circumstances the energy put into the system is transformed into both heat and work energy. This means that it would take more energy to heat a constant pressure system by the same amount as a constant volume system.

5. What are the values for:

a.  $C_v = \frac{3}{2} R$

b.  $C_p = C_v + R = \frac{5}{2} R$

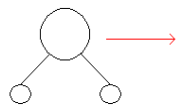
Where  $R = 8.3145 \text{ J / mol K}$

6. Why is  $C_v < C_p$ ?

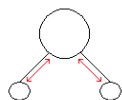
$C_p > C_v$  because energy gets used for heating and work in constant pressure situation. Therefore you need the more energy for the same change in temperature.

7. When energy is added to a molecule there are three potential forms of motion that it can be transferred into:

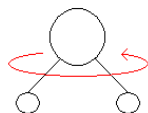
a. **Translational** – The molecule's movement around the container



b. **Vibrational** – The spring-like movement of the bond between atoms.



c. **Rotational** – The spinning of the molecule on an axis.



8. **Translational motion** is the only motion that directly affects temperature.

9. The values  $\frac{3}{2} R$  and  $\frac{5}{2} R$  are only applicable to **monatomic** ideal gases. Why?

A monatomic ideal gas is only capable of undergoing translational motion. Meaning that all the energy that goes to molecule (excluding the work aspect) goes towards a motion that will directly increase the temperature. Gases with more than one atom are able to undergo rotational and

vibrational motion as well. Because these 2 additional types of motion do not lend to an increase in temperature... more energy has to be put into compensate for the loss.

10. This means that the calculated molar heat capacities are often **less** than actual molar heat capacities.

11. What equation relates  $\Delta E$  to heat capacity?

$$\Delta E = n C_v \Delta T$$

a. Under what conditions can you use this equation?

Under any all conditions.  $\Delta E$  is always tied to  $C_v$ .

b. Under what conditions does  $\Delta E = q$ ?

When the volume is constant.

12. What equation relates  $\Delta H$  to heat capacity?

$$\Delta H = n C_p \Delta T$$

a. Under what conditions can you use this equation?

Under any all conditions.  $\Delta H$  is always tied to  $C_p$ .

b. Under what conditions does  $\Delta H = q$ ?

When the pressure is constant.

13. Which value of R do we use in these equations?

$$R = 8.3145 \frac{\text{J}}{\text{mol K}}$$

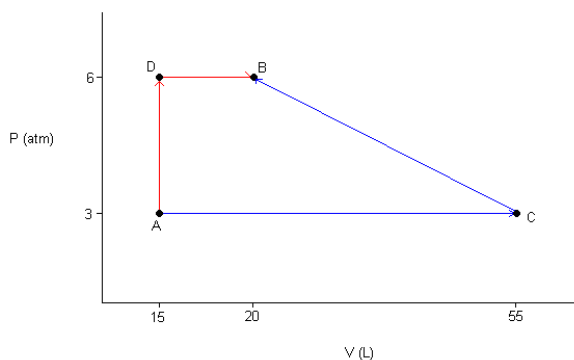
14. Fill in the chart.

|            | Constant Pressure   | Constant Volume                      |
|------------|---|--------------------------------------|
| q          | $q = nC_p\Delta T$<br>$\Delta H = q$  | $q = nC_v\Delta T$<br>$\Delta E = q$ |
| w          | $w = -P\Delta V$ (when volume changes)<br>$w = -nR\Delta T$ (when temp. changes)<br>$w = -RT\Delta n$ (when moles change) | $w = 0$                              |
| $\Delta E$ | $E = nC_v\Delta T$<br>$E = q + w$   |                                      |
| $\Delta H$ | $H = nC_p\Delta T$<br>$H = E + \Delta(PV)$  |                                      |

15. Consider a sample containing 5 moles of a monatomic ideal gas that is taken from State A  $\rightarrow$  State B by 2 different paths. For each step, assume that the external P is constant and equals the final P of the gas for that step. Calculate the values of q, w,  $\Delta H$  and  $\Delta E$  for each step along the 2 paths and the totals for the 2 paths. What do the totals demonstrate?

a.  $(P_A=3\text{atm}, V_A=15\text{L}) \rightarrow (P_C=3\text{atm}, V_C=55\text{L}) \rightarrow (P_B=6\text{atm}, V_B=20\text{L})$

b.  $(P_A=3\text{atm}, V_A=15\text{L}) \rightarrow (P_C=6\text{atm}, V_C=15\text{L}) \rightarrow (P_B=6\text{atm}, V_B=20\text{L})$



Path A

**A → C**

The pressure is constant along this path. This tells us some important information. First it establishes which of the equations for q we will use. We also know that under constant pressure circumstances  $q = \Delta H$ . So we know that the answer get applies to both.

$$q = nC_p\Delta T = \Delta H$$

In this question they did not give us any information about the change in temperature. But because we are dealing with an ideal gas, we can use the ideal gas law to solve for the temperature at point A and point C. We can then use those values to solve for  $\Delta T$ .

$$T_A = \frac{PV}{nR} = \frac{(3 \text{ atm})(15\text{L})}{(5 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{mol K}})} = 109.7 \text{ K}$$

$$T_C = \frac{PV}{nR} = \frac{(3 \text{ atm})(55 \text{ L})}{(5 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{mol K}})} = 402.1 \text{ K}$$

That means that

$$\Delta T = (402.1 \text{ K} - 109.7 \text{ K}) = 292.4 \text{ K}$$

Now we can plug in and solve:

$$\Delta H = q = (5 \text{ mol}) \left( \frac{5}{2} \right) (8.3145 \frac{\text{J}}{\text{mol K}}) (292.4 \text{ K}) \left( \frac{\text{kJ}}{1000\text{J}} \right) = \boxed{30.4 \text{ kJ}}$$

Remember there are two values for R

In the Ideal Gas Law:

$$R = 0.08206 \frac{\text{Latm}}{\text{mol K}}$$

In all other equations:

$$R = 8.3145 \frac{\text{J}}{\text{mol K}}$$

Now, let's turn our attention to work.

$$w = -P\Delta V = - (3 \text{ atm})(55\text{L} - 15\text{L}) = -120 \text{ L atm}$$

$$-120 \text{ L atm} \left( \frac{0.101325 \text{ kJ}}{\text{L atm}} \right) = \boxed{-12.2 \text{ kJ}}$$

Lastly, we will solve for  $\Delta E$ . We could use either  $\Delta E = nC_v\Delta T$  or  $\Delta E = q + w$ . Because we have already solved for  $q$  and  $w$ , I will use the latter.

$$\Delta E = q + w = (30.4 \text{ kJ}) + (-12.2 \text{ kJ}) = \boxed{18.2 \text{ kJ}}$$

Now we perform the same calculations for the second step on the path.

### C $\rightarrow$ B

There isn't a constant along this path. That means that we cannot use the equations we have for  $q$ . Both of the equations require something to be held constant. So we will start with work.

$$w = -P\Delta V = -(6 \text{ atm})(20 \text{ L} - 55 \text{ L}) = 210 \text{ L atm}$$

$$210 \text{ L atm} \frac{0.101325 \text{ kJ}}{\text{L atm}} = \boxed{21.3 \text{ kJ}}$$

I knew to use 6 atm for the pressure because the question stated "assume that the external  $P$  is constant and equals the final  $P$  of the gas for that step".

Next, let's solve for  $\Delta E$ . Remember that, regardless of the conditions of the reaction, we can always use

$$\Delta E = nC_v\Delta T$$

First, we must use the ideal gas law to obtain the relevant temperatures at point C and point B to solve for  $\Delta T$ .

$$T_C = \frac{PV}{nR} = \frac{(3 \text{ atm})(55 \text{ L})}{(5 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{mol K}})} = 402.1 \text{ K}$$

$$T_B = \frac{PV}{nR} = \frac{(6 \text{ atm})(20 \text{ L})}{(5 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{mol K}})} = 292.5 \text{ K}$$

Now we can solve for  $\Delta T$

$$\Delta T = 292.5 \text{ K} - 402.1 \text{ K} = -109.6 \text{ K}$$

Now we can plug into the expression for  $E$  and solve

$$\Delta E = (5 \text{ mol}) \left( \frac{3}{2} \right) (8.3145 \frac{\text{J}}{\text{mol K}}) (-109.6 \text{ K}) \left( \frac{\text{kJ}}{1000\text{J}} \right) = \boxed{-6.83 \text{ kJ}}$$

$$\Delta E = q + w \rightarrow q = \Delta E - w$$

Plugging in our values, we get

$$q = (-6.83 \text{ kJ}) - (21.3 \text{ kJ}) = \boxed{-28.1 \text{ kJ}}$$

Lastly, we will solve for  $\Delta H$  using the equation

$$\Delta H = nC_p\Delta T$$

Remember, this equation can be used regardless of conditions. Because we already solved for  $\Delta T$  from C  $\rightarrow$  B we can just plug into the equation and solve.

$$\Delta H = (5 \text{ mol}) \left( \frac{5}{2} \right) (8.3145 \frac{\text{J}}{\text{mol K}}) (-109.6 \text{ K}) \left( \frac{\text{kJ}}{1000\text{J}} \right) = \boxed{-11.4 \text{ kJ}}$$

### Path B

#### **A $\rightarrow$ D**

The volume is constant along this path. This information tells us some important facts. First, because there is no change in volume, there is no work, i.e.  $w = 0$ . This establishes that  $\Delta E = q$ . Thus we will start our calculations using:

$$q = \Delta E = nC_v\Delta T$$

Once again our first step is to determine the temperatures at point A and point D in order to determine  $\Delta T$ .

$$T_A = \frac{PV}{nR} = \frac{(3 \text{ atm})(15\text{L})}{(5 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{mol K}})} = 109.7 \text{ K}$$

$$T_D = \frac{PV}{nR} = \frac{(6 \text{ atm})(15\text{L})}{(5 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{mol K}})} = 219.4 \text{ K}$$

Thus

$$\Delta T = (219.4\text{K} - 109.7 \text{ K}) = 109.7\text{K}$$

We can now plug into the equation and solve for  $\Delta E$  and  $q$ .

$$q = \Delta E = nC_v\Delta T = (5 \text{ mol})^{3/2} (8.3145 \frac{\text{J}}{\text{mol K}}) (109.7\text{K}) (\frac{\text{kJ}}{1000 \text{ J}}) = \boxed{6.84 \text{ kJ}}$$

Lastly, we can solve for  $\Delta H$  using

$$\Delta H = nC_p\Delta T$$

Plugging in we get

$$\Delta H = nC_p\Delta T = (5 \text{ mol})^{5/2} (8.3145 \frac{\text{J}}{\text{mol K}}) (109.7\text{K}) (\frac{\text{kJ}}{1000 \text{ J}}) = \boxed{11.4 \text{ kJ}}$$

### D → B

The pressure is constant along this path. This tells us some important information. First it establishes which of the equations for  $q$  we will use. We also know that under constant pressure circumstances  $q = \Delta H$ . So we know that the answer we get applies to both.

$$q = \Delta H = nC_p\Delta T$$

Once again our first step is to determine the temperatures at point D and point B in order to determine  $\Delta T$ .

$$T_D = \frac{PV}{nR} = \frac{(6 \text{ atm}) (15\text{L})}{(5 \text{ mol}) (0.08206 \frac{\text{L atm}}{\text{mol K}})} = 219.4 \text{ K}$$

$$T_B = \frac{PV}{nR} = \frac{(6 \text{ atm}) (20 \text{ L})}{(5 \text{ mol}) (0.08206 \frac{\text{L atm}}{\text{mol K}})} = 292.5 \text{ K}$$

Thus

$$\Delta T = (292.5\text{K} - 219.4 \text{ K}) = 73.1 \text{ K}$$

Now we can plug in and solve

$$q = \Delta H = nC_p\Delta T = (5 \text{ mol})^{5/2} (8.3145 \frac{\text{J}}{\text{mol K}}) (73.1 \text{ K}) (\frac{\text{kJ}}{1000 \text{ J}}) = \boxed{7.6 \text{ kJ}}$$

Next we turn our attention to work.

$$w = - P\Delta V = - (6\text{atm}) (20\text{L} - 15\text{L}) = -30 \text{ L atm}$$

$$-30 \text{ L atm} \frac{0.101325 \text{ kJ}}{\text{L atm}} = \boxed{-3.04 \text{ kJ}}$$



Lastly, we will solve for  $\Delta E$ . We could use either  $\Delta E = nC_v\Delta T$  or  $\Delta E = q + w$ . Because we have already solved for  $q$  and  $w$ , I will use the latter.

$$\Delta E = (7.6 \text{ kJ}) + (-3.04 \text{ kJ}) = \boxed{4.6 \text{ kJ}}$$

| Totals  |   |
|---|---|
| Path A  | Path B  |
| $q = (30.4 \text{ kJ}) + (-28.1 \text{ kJ}) = 2.3 \text{ kJ}$         | $q = (6.84 \text{ kJ}) + (7.6 \text{ kJ}) = 14.4 \text{ kJ}$        |
| $w = (-12.2 \text{ kJ}) + (21.3 \text{ kJ}) = 9.1 \text{ kJ}$         | $w = (0 \text{ kJ}) + (-3.04 \text{ kJ}) = -3.04 \text{ kJ}$        |
| $\Delta E = (18.2 \text{ kJ}) + (-6.83 \text{ kJ}) = 11.4 \text{ kJ}$ | $\Delta E = (6.84 \text{ kJ}) + (4.6 \text{ kJ}) = 11.4 \text{ kJ}$ |
| $\Delta H = (30.4 \text{ kJ}) + (-11.4 \text{ kJ}) = 19.0 \text{ kJ}$ | $\Delta H = (11.4 \text{ kJ}) + (7.6 \text{ kJ}) = 19.0 \text{ kJ}$ |

As you can see from the totals. The values of  $q$  and  $w$  are path dependent. But the values of  $\Delta H$  and  $\Delta E$  are path independent – exactly the same totals were obtained for path A and path B.