

1.6 Heat Capacity

Heat capacity is proportionality constant between Q and ΔT

$$C \equiv \frac{Q}{\Delta T}$$

C is proportional to amount of material $C = c \cdot m$
specific heat capacity $\swarrow$
mass of object $\nwarrow$

This definition is ambiguous because could be doing work on object at same time

$$C = \frac{\Delta U - W}{\Delta T} = \frac{\Delta U}{\Delta T} - \frac{W}{\Delta T}$$

$$C_v = \text{heat capacity at constant volume} \Rightarrow W=0 \\ = \left(\frac{\partial U}{\partial T} \right)_v$$

Often object expands when heat is added so $W = -P\Delta V$

$$C_p = \text{heat capacity at constant pressure} \\ = \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

For solids and liquids $\frac{\partial V}{\partial T}$ is usually small so $C_p \approx C_v$

For gasses C_p and C_v substantially differ.

$$U = N f \frac{1}{2} k_B T \Rightarrow \frac{\partial U}{\partial T} = \frac{1}{2} N f k_B = C_v$$

See Figs 1.13 and 1.14 page 30 for C_v as fct. of T

$$\text{For ideal gas } V = \frac{N k_B T}{P} \Rightarrow P \left(\frac{\partial V}{\partial T} \right)_p = N k_B$$

$$C_p = \left(\frac{f}{2} + 1 \right) N k_B = \frac{f+2}{2} N k_B = C_v + N k_B = C_v + nR$$

$$\text{For ideal gas } C_p - C_v = N k_B = nR$$

Prob 1.43 $C_v = 4.2 \frac{\text{J}}{\text{K}}$ for $1\text{g} = \frac{1}{18} \text{mol} = 3.34 \times 10^{22} \text{molecules}$

$$C_v/\text{molecule} = 1.26 \times 10^{-22} \frac{\text{J}}{\text{K}} = 9.1 k_B = \frac{f}{2} k_B \quad f = 18??$$

Partial derivatives holding different quantities fixed is important

Examples $F = r^2 z$ $r s z = 5$

$$\left(\frac{\partial F}{\partial r}\right)_z = 2rz \quad \left(\frac{\partial F}{\partial r}\right)_s = \frac{\partial}{\partial r} \left(r^2 \frac{5}{rs}\right) = \frac{5}{s}$$

$$= 2/5 \neq 5/5$$

Prob 1.41

$$Q_{\text{metal}} + Q_{\text{H}_2\text{O}} = 0$$

$$C_{\text{metal}} (24^\circ\text{C} - 100^\circ\text{C}) + C_{\text{H}_2\text{O}} (24^\circ\text{C} - 20^\circ\text{C})$$

$$C_{\text{metal}} (-76^\circ\text{C}) + 250\text{g} \frac{4.2 \frac{\text{J}}{\text{K}}}{4200 \frac{\text{J}}{\text{K}}} 4^\circ\text{C} = 0 \quad C_{\text{metal}} = 55 \frac{\text{J}}{\text{K}}$$

$$C_{\text{metal}} = \frac{55 \frac{\text{J}}{\text{K}}}{100\text{g}} = 0.55 \frac{\text{J}}{\text{K} \cdot \text{g}}$$

Latent Heat — at phase transition, $Q \neq 0$ but $\Delta T = 0$ until all material has made transition

At the transition $L \equiv \frac{Q}{m}$
↗ latent heat ↖ heat added
↖ amount of material that made transition

You have 1 kg ice at 0°C , you add 333J and melt 1g.
 If you add 333J to 2 kg ice at 0°C , how much melts?

+ variations

Enthalpy!! $H \equiv U + PV$

work needed to make room for the system at constant P

Look at change in H if do something to system at constant P ,

$$U + \Delta U + P(V + \Delta V) = U + PV + \Delta U + P\Delta V \\ = H + \Delta H$$

If only compressional work allowed

$$\Delta U = Q + W \\ = Q - P\Delta V$$

$$\Rightarrow \boxed{Q = \Delta H}!!$$

If there are other processes doing work,

$$\Delta H = Q + W_{\text{other}} \\ \quad \quad \quad \nwarrow \text{not compression}$$

This leads to another definition $C_p = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$

Remember $C_v = \left(\frac{\partial U}{\partial T}\right)_V$

Note $\Delta H = \Delta U + P\Delta V$ means enthalpy can increase/decrease either because internal energy increases or system expands/contracts and does work on environment.

* Important * The latent heat of transformation is equal to the change in enthalpy!!

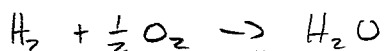
$$\Delta H = \Delta U + P\Delta V = Q \text{ for transformation because} \\ \quad \quad \quad \nwarrow \text{work done on atmosphere during transformation} \\ \quad \quad \quad \text{transformation takes place at constant } P$$

For example boiling water $\Delta V = V_{\text{steam}} - V_{\text{water}} \approx V_{\text{steam}}$

$$P\Delta V \approx P \cdot V = 1 \text{ mol } R T = 1 \text{ mol } 8.31 \frac{\text{J}}{\text{mol K}} 373 \text{ K} = 3100 \text{ J} = \text{work on atmosphere}$$

$$Q = \Delta H = 40,660 \text{ J for boiling 1 mol of water}$$

$$\Rightarrow 37,560 \text{ J in } \Delta U$$

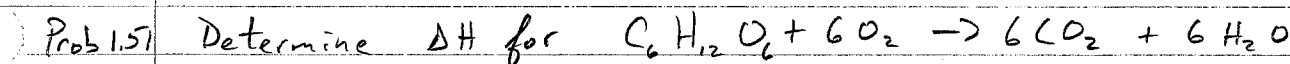


Look in table on page 405 $\Delta_f H$ for H_2O liquid
 $\Delta_f H = -285.83 \times 10^3 \text{ J}$ for 1 mol

Note for $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$, the original V is $\sim \frac{3}{2} \times$ the final V so you get some energy from atmosphere doing work to collapse volume if H_2O is gas and original V is $\gg$ than final V if going to liquid.

Prob 1.49 The final Volume ≈ 0 $P \Delta V = -1.01 \times 10^5 \text{ Pa } V_{\text{init}}$
 $= -1.5 \text{ mol} \cdot 8.31 \frac{\text{J}}{\text{mol K}} \cdot 298 \text{ K} = -3.7 \times 10^3 \text{ J}$
 $\Delta U = -285.8 \times 10^3 \text{ J} - P \Delta V = -282.1 \times 10^3 \text{ J} = -282.1 \text{ kJ}$

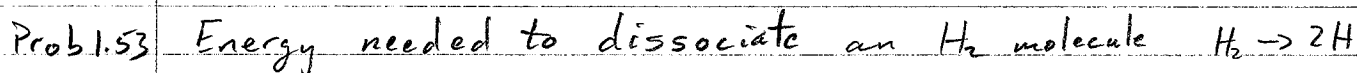
Important: Table on 404-405 is at 298 K



1st Check # of atoms start 6C, 12H, 18O
 final 6C, 12H, 18O

From table

$\text{C}_6\text{H}_{12}\text{O}_6$	$\Delta H = -1273 \text{ kJ}$	$\Delta H_{\text{tot}} = \Delta H_{\text{fin}} - \Delta H_{\text{init}}$ $= 6(-393.5 \text{ kJ}) + 6(-285.8 \text{ kJ}) - (-1273 \text{ kJ}) - 0$ $= -2803 \text{ kJ}$
O_2	$\Delta H = 0$	
$\text{H}_2\text{O}(\text{l})$	$\Delta H = -285.8 \text{ kJ}$	
$\text{CO}_2(\text{g})$	$\Delta H = -393.5 \text{ kJ}$	



$\text{H}_2(\text{g})$	$\Delta H = 0$	$\Delta H_{\text{tot}} = \Delta H_{\text{fin}} - \Delta H_{\text{init}} = 2(217.97 \text{ kJ}) - 0$ $= 435.9 \text{ kJ}$
$\text{H}(\text{g})$	$\Delta H = 217.97 \text{ kJ}$	

To find energy to dissociate 1 atom need ΔU
 $\Delta U = \Delta H - P \Delta V$

The gas goes from 1 mole to 2 moles of objects

$$\Rightarrow P \Delta V = 1 \text{ mol } R T = 1 \text{ mol } 8.31 \frac{\text{J}}{\text{mol K}} \cdot 298 \text{ K} = 2476 \text{ J} = 2.5 \text{ kJ}$$

$$\Delta U = 435.9 \text{ kJ} - 2.5 \text{ kJ} = 433.4 \text{ kJ}$$

$$\text{Energy to dissociate 1} = \frac{433.4 \times 10^3 \text{ J}}{6.02 \times 10^{23}} = 7.20 \times 10^{-19} \text{ J} = 4.49 \text{ eV}$$