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 $C = \overset{\text{specific heat capacity}}{c} \cdot \underset{\text{mass of object}}{m}$

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 = 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 = 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 $C_P \cong C_V$

For gasses C_P and C_V substantially differ.

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

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

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

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

For ideal gas $C_P - C_V = N k_B = nR$

Prob 1.43 $C_V = 4.2\ \mathrm{J}/{}^\circ\mathrm{C}$ for $1\,\mathrm{g} = \frac{1}{18}\ \mathrm{mol} = 3.34 \times 10^{22}$ molecules

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

Partial derivatives holding different quantities fixed is important

Examples $\quad F = r^2 z \qquad rsz = 5$

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

Prob 1.41

$$Q_{metal} + Q_{H_2O} = 0$$
$$C_{metal}(24^\circ\mathrm{C} - 100^\circ\mathrm{C}) + C_{H_2O}(24^\circ\mathrm{C} - 20^\circ\mathrm{C})$$
$$C_{metal}(-76^\circ\mathrm{C}) + \underbrace{250\,\mathrm{g}\ 4.2\frac{\mathrm{J}}{{}^\circ\mathrm{C}\,\mathrm{g}}\ 4^\circ\mathrm{C}}_{4200\,\mathrm{J}} = 0 \qquad C_{metal} = 55\ \frac{\mathrm{J}}{{}^\circ\mathrm{C}}$$
$$c_{metal} = \frac{55}{100\,\mathrm{g}}\ \frac{\mathrm{J}}{{}^\circ\mathrm{C}} = 0.55\ \frac{\mathrm{J}}{{}^\circ\mathrm{C}\ \mathrm{g}}$$

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

At the transition $\underbrace{L}_{\text{latent heat}} \equiv \dfrac{\overset{\text{heat added}}{Q}}{\underset{\text{amount of material that made transition}}{m}}$

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

+ variations

Enthalpy!! $H \equiv U + \underbrace{PV}_{\text{work needed to make room for the system at constant } P}$

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,

$$\Delta H = Q + W_{other}$$
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!!

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

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

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

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

$\Rightarrow 37{,}560\,J$ in ΔU

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Look in table on page 405 $\Delta_f H$ for H_2O liquid

$\Delta_f H = -285.83 \times 10^3$ J for 1 mol

Note for $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, the original V is $\approx \frac{3}{2}\times$ the final V so you get some energy from atmosphere doing work to collapse volume if H_2O is gas and original V is >> than final V if going to liquid.

Prob 1.49 The final Volume ≈ 0 $\quad P\Delta V = -1.01\times10^5\,\text{Pa}\;V_{init}$

$= -1.5\,\text{mol}\cdot 8.31\frac{\text{J}}{\text{mol K}}\,298\text{K} = -3.7\times10^3\,\text{J}$

$\Delta U = -285.8\times10^3\,\text{J} - P\Delta V = -282.1\times10^3\,\text{J} = -282.1\,\text{kJ}$

Important: Table on 404-405 is at 298 K

Prob 1.51 Determine ΔH for $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

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

final 6C, 12H, 18O

From table

$C_6H_{12}O_6$ $\quad \Delta H = -1273$ kJ $\qquad \Delta H_{TOT} = \Delta H_{fin} - \Delta H_{init}$

O_2 $\quad \Delta H = 0$ $\qquad = 6(-393.5\,\text{kJ}) + 6(-285.8\,\text{kJ}) - (-1273\,\text{kJ}) - 0$

$H_2O(l)$ $\quad \Delta H = -285.8$ kJ $\qquad = \underline{-2803\,\text{kJ}}$

$CO_2(g)$ $\quad \Delta H = -393.5$ kJ

Prob 1.53 Energy needed to dissociate an H_2 molecule $\quad H_2 \rightarrow 2H$

$H_2(g)$ $\quad \Delta H = 0$

$H(g)$ $\quad \Delta H = 217.97$ kJ $\qquad \Delta H_{TOT} = \Delta H_{fin} - \Delta H_{init} = 2(217.97\,\text{kJ}) - 0$

$= 435.9$ 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

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

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

Energy to dissociate 1 $= \frac{433.4\times10^3\,\text{J}}{6.02\times10^{23}} = 7.20\times10^{-19}\,\text{J} = 4.49\,\text{eV}$