Heat Capacity of Gases at Constant Pressure: $C_p$

What happens if we heat the gas while keeping $p = p_{ext} = \text{constant} = 1 \text{ bar}$?

But, expansion does some work, which has a cooling effect. $\Delta T$ is smaller. $C = q/\Delta T$, so $C$ is larger.

More heat will be needed to raise the temperature than if volume is kept constant.

$C_p > C_v$, always

Heating make the molecules move faster, making the pressure increase, which causes expansion.

$pV = nRT$
$p\Delta V = nR\Delta T$
How much more heat is required?

\[ H = U + pV \]

what is \( pV? \)

\( pV = nRT \) if ideal gas

but \( dH = dq \) (if \( p=p_{\text{ext}} \) and only \( pV \) work possible)

\[
\frac{dH}{dT} = \frac{dq}{dT} \quad \text{if pressure is constant = p external}
\]

\[
\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial q}{\partial T} \right)_p = C_p, \text{ in proper notation}
\]

\[
\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial (U + PV)}{\partial T} \right)_p = \left( \frac{\partial (U + nRT)}{\partial T} \right)_p = \left( \frac{\partial (U)}{\partial T} \right)_p + nR
\]

\[
\text{but} \left( \frac{\partial (U)}{\partial T} \right)_p = \left( \frac{\partial (U)}{\partial T} \right)_V = C_V \text{ because } U \text{ depends only on } T
\]

Giving \( C_p = C_V + nR \) for ideal gases
Very very high pressure applied to a solid will often turn it into another crystal form that is more dense, e.g., graphite into diamond.
Heats of CHEMICAL REACTIONS ($\Delta_r H$)  
(and Phase Changes treated the \textit{same} way) 

\begin{align*} 
\text{State 1} & \rightarrow \text{State 2} \\
\text{Reactants} & \rightarrow \text{Products} \\
\text{Tabulated at 1 bar and some T (usually 298 K)} \\
\text{(note that this is constant T and p)} \\
\text{so, } q & = q_p = \Delta H \\
\end{align*}

\textit{In general:} if weak bonds $\rightarrow$ STRONG BONDS then the reaction is \text{very EXOTHERMIC} $==$ “chemical energy” 

\[ \Delta_r H = \Sigma H_i(\text{products}) - \Sigma H_i(\text{reactants}) \]

\text{(this is an abstract useless statement)} 

\textit{In practice, we use a Table standard heats of formation} 

\[ \Delta_r H^0 = \Sigma \Delta_f H^0_{298} (\text{products}) - \Sigma \Delta_f H^0_{298} (\text{reactants}) \]
From a table of $\Delta_r H^0_{298}$ for a few dozen reactions we can **know** the $\Delta_r H^0$ for **thousands** of reactions that may have never been measured.
Consider a generic chemical reaction
\[ aA + bB \rightarrow cC + dD \]
where the \( a, b, c, d \) = the stoichiometric numbers
and \( A, B, C, D \) are chemicals.

\[ \Delta_r H^0 = c \Delta_f H^0(C) + d \Delta_f H^0(D) - a \Delta_f H^0(A) - b \Delta_f H^0(B) \]

Example:

\[ C_6H_{12}O_6(s) + 6O_2 \rightarrow 6CO_2(g) + 6H_2O(g) \]

\[ \begin{array}{cccc}
-1274.4 & 0 & -393.5 & -241.8 \\
\end{array} \]

\[ \Delta_r H^0 \] kJ mol\(^{-1}\)

\[ \Delta_r H^0 = 6 \times (-393.5) + 6 \times (-241.8) - \left( -1274.4 + 6 \times 0 \right) \]

\[ = -2537.4 \text{ kJ/mol as written} \]

you **MUST** always associate the \( \Delta_r H^0 \) with a balanced reaction.
What EXACTLY is $\Delta_f H^0_{298}$ ???

$\Delta_f H^0_{298} =$ **Standard Heat of Formation** (at $25^\circ$ C)

The superscript 0 means that all reactants and products are in their **standard state**, which means:

- **Gases:** 1 bar and **ideal**
- **Liquids and solids:** 1 bar applied and **pure**
- **Solutes:** 1 molar (usually) and **ideal** (*no solute-solute interaction*)

*Note that temperature is NOT part of the definition.* *(There is a different table for every temperature.)*

$\Delta_f$ means **formation of 1 mole** from the **most stable** form of the **elements** at the given temperature (298 in this case)

-----------------------------------------------

**Quiz:** What chemical reaction has:

1. $\Delta H_{298} = \Delta_f H^0_{298}$ for $\text{H}_2\text{O (g)}$  
   $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O(g)}$

2. $\Delta H_5 = \Delta_f H^0_5$ for $\text{H}_2\text{O (g)}$  
   $\text{H}_2(s) + \frac{1}{2}\text{O}_2(s) \rightarrow \text{H}_2\text{O(g)}$

3. Why is $\Delta_f H^0_{298} = 0$ for $\text{H}_2(g)$, $\text{O}_2(g)$, $\text{N}_2(g)$ ...?  
   $\text{H}_2(g) \rightarrow \text{H}_2(g)$
We will constantly be using: Powerful Exploitation of State Function Concept in Thermodynamics

Path does not matter: $H$ is a STATE FUNCTION

\[ \Delta H_{\text{unknown}} = \Delta H_1 + \Delta H_2 \]

When applied to chemical reactions this trick is known as Hesses Law
We will constantly be using:

Powerful Exploitation of State Function Concept in Thermodynamics

Path does not matter: \( H \) is a STATE FUNCTION

\[ \Delta H^0_{\text{unknown}} = \pm \sum \Delta H_f^0 \text{ (prod)} - \sum \Delta H_f^0 \text{ (react)} \]
“Bond Dissociation Energies”
Another Exploitation of State Function Concept in Thermodynamics

Path does not matter: $H$ is a STATE FUNCTION

$$\Delta H^0_{\text{unknown}} = \sum \text{bond energies (react.)} - \sum \text{bond energies (prod.)}$$
### Bond Dissociation Energies (Enthalpies)

**Table 2.3** Average bond dissociation energies at 25°C

<table>
<thead>
<tr>
<th>Bond</th>
<th>$D$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>344</td>
</tr>
<tr>
<td>C═C</td>
<td>615</td>
</tr>
<tr>
<td>C≡C</td>
<td>812</td>
</tr>
<tr>
<td>C—H</td>
<td>415</td>
</tr>
<tr>
<td>C—N</td>
<td>292</td>
</tr>
<tr>
<td>C—O</td>
<td>350 securities</td>
</tr>
<tr>
<td>C═O</td>
<td>725 securities</td>
</tr>
<tr>
<td>C—S</td>
<td>259</td>
</tr>
<tr>
<td>N—H</td>
<td>391</td>
</tr>
<tr>
<td>O—O</td>
<td>143 securities</td>
</tr>
<tr>
<td>O—H</td>
<td>463 securities</td>
</tr>
<tr>
<td>S—H</td>
<td>339</td>
</tr>
<tr>
<td>H$_2$</td>
<td>436.0</td>
</tr>
<tr>
<td>N$_2$</td>
<td>945.4 <strong>Very Strong</strong></td>
</tr>
<tr>
<td>O$_2$</td>
<td>498.3</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>716.7</td>
</tr>
</tbody>
</table>

**ESTIMATING \( \Delta H \) FROM BOND ENERGIES**

Scheme:  
1. Reactants → \( \text{gaseous Atoms} \) → \( \text{gaseous Atoms} \)
2. Products

\[
\text{C}_4\text{H}_6(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g}) + 4\text{O}(\text{g})
\]

\[
\text{C}(\text{g}) + 4\text{H}(\text{g}) + 4\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})
\]

\[
\text{H}_2\text{C} = \text{O} + \text{O} = \text{O}
\]

\[
\text{H} - \text{C} - \text{H} \rightarrow \text{H} - \text{C} = \text{O} - \text{H}
\]

- Weak bonds
- Strong bonds

\[
\Delta H \approx 2\text{ BE}(O=O) + 4\text{ BE}(C-H) - 2\text{ BE}(O=O) - 4\text{ BE}(O=H)
\]

\[
\approx 2(498) + 4(415) - 2(725) - 4(463)
\]

\[
\approx -646 \text{kJ/mol} \quad \text{20\% error}
\]

Exact from \( \Delta H^\circ = -802.3 \text{kJ/mol} \)

(The glass is 80\% FULL) 😊
Finding $\Delta U$ of a reaction

$\Delta H = \Delta U + \Delta (PV)$
$\Delta U = \Delta H - \Delta (PV)$

Ignore volume of solids and liquids

Then $\Delta U = \Delta H - \Delta (nRT) = \Delta H - \Delta n(RT)$

because $T$ is constant

where $\Delta n$ is the change of moles of gases only.