A quote of the week
(or camel of the week):

There is no expedience to which a man will not go to avoid the labor of thinking.

Thomas A. Edison
**Hess law. Algorithm**

1. Select a reaction, possibly containing specific compounds from reaction T.

2. Is the reaction obtained the same as reaction T?
   - Yes: Go to E.
   - No: Select another reaction and add it to (subtract from) the one already obtained.

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Physical Chemistry EPM/02
More about enthalpy

Change in enthalpy of a system, where no chemical reaction occurs (only physical changes, like heating or cooling, expansion or compression) is given by:

\[ dh = nC_p dT; \quad dH = C_p dT \]

Hence:

\[ C_p = \frac{dH}{dT} = \left( \frac{dQ}{dT} \right)_P \]

Enthalpy can change in any type of process, whilst only in isobaric processes it is equal to the heat exchanged.
Internal energy

When heat is exchanged at constant volume (in an isovolumic or isochoric process), this heat is equal to the change in yet another state function, known as internal energy of the system:

\[ du = nC_v \, dT; \quad dU = C_v \, dT \]

Hence:

\[ C_v = \frac{dU}{dT} = \left( \frac{dQ}{dT} \right)_V \]

Internal energy can change in any type of process, whilst only in isovolumic processes it is equal to the heat exchanged.
**$C_P$ and $C_V$**

We will discuss it later in details, but for the time being, let’s assume that for the perfect (ideal gas):

<table>
<thead>
<tr>
<th>gas molecule</th>
<th>$C_V$</th>
<th>$C_P = C_V + R$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>monoatomic</td>
<td>$3/2R$</td>
<td>$5/2R$</td>
<td>$5/3 = 1.67$</td>
</tr>
<tr>
<td>diatomic</td>
<td>$5/2R$</td>
<td>$7/2R$</td>
<td>$7/5 = 1.40$</td>
</tr>
</tbody>
</table>

$$\kappa = \frac{C_P}{C_V} \quad P_1V_1^\kappa = P_2V_2^\kappa = \text{const}; \quad \left(\frac{V_1}{V_2}\right)^{\kappa - 1} = \frac{T_2}{T_1}$$

The last column shows the coefficient of the equation of reversible adiabatic process (Poisson’s equation).
**Internal energy (2)**

**Internal energy** is the sum of all kinds of energy contributing to the overall energy of the system.

Internal energy of the isolated system is constant.

This is the first law of thermodynamics !!!

In the case of a closed system, when energy can be exchanged, internal energy can change, too. Its change is always equal to:

\[ du = dq + dw; \quad \Delta u = q + w \]

A system contradictory to the first law (first principle) is called *perpetuum mobile*. 
**Internal energy (3)**

\[ du = dq + dw; \quad \Delta u = q + w \]

where: \( q \) stands for heat and \( w \) represents work (energy exchanged as heat and as work).

As you can see, after integration, the finite changes in the two values are written without the \( \Delta \) sign, because they cannot be calculated as differences between their final and initial values, respectively. **Heat and work are not state functions** (state properties).

Therefore, the two quantities (esp. work) must be calculated separately.
**Work of expansion**

We begin our considerations with systems exchanging energy with their surroundings in the form of mechanical energy due to the change of system volume. This is important, first of all, in gaseous systems.

Expansion is any process when \( dV > 0 \). The same process reversed is known as compression \( (dV < 0) \). Work of expansion may be calculated as:

\[
\begin{align*}
dw &= -P_{\text{ext}} \, dV; \\
w &= -\int P_{\text{ext}} (V) \, dV
\end{align*}
\]

The minus sign is added, because an expanding system is doing work (losing energy), while we do compress the system, delivering energy to it.
Work of expansion (2)

A process may be treated as reversible, when the changes occur at a very slow pace (infinitely slow). It can be treated as a series of states of equilibrium. Sometimes such processes are known as „quasi-static” processes.

One would ask, why should we be interested in such strange phenomena? The answer is that the values of heat and work in reversible processes are reach maximum (absolute) values.

In reversible processes external pressure is practically the same as the pressure of the gas in the system.

\[ P_{\text{ext}} = P \pm dP \]
The cylinder here is „transparent”, so we can see the movements of the piston. The piston closes the cylinder tightly, though it can move without friction, and it is weightless. Here, volume is changed by $dV$, while the piston shifts by $dx$. The walls of the cylinder and the piston may be either adiabatic or diathermic.
Work of expansion (4)

Let’s consider several cases of expansion:

1. Expansion to vacuum (external pressure is equal to zero). If we use the term „final pressure” it simply means that some kind of stopper was set to block the movement of the piston.

\[ P_{ext} = 0 \]

\[ w = \int_{init}^{fin} dw = -P_{ext} \int_{i}^{f} dV = 0 \]
**Work of expansion (5)**

2. Expansion against a constant external pressure. Again, final gas pressure (must be greater or equal to the external pressure) results from blocking the movement of the piston at certain position.

\[ P_{\text{ext}} \neq 0 = \text{const} \]

\[
    w = \int_{\text{init}}^{\text{fin}} dw = -P_{\text{ext}} \int_{i}^{f} dV = -P_{\text{ext}} (V_k - V_i) = -P_{\text{ext}} \Delta V
\]

The same is true for a reversible isobaric transition.

\[ w = -P \Delta V \]
Work of expansion (6)

3. Reversible (quasi-static) isothermal transition: $P_{ex} = P \pm dP$

$$dw = -P_{ex}dV = -PdV = -\frac{nRT}{V}dV$$

$$w = \int_{i}^{f} dw = -nRT \int_{i}^{f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$w = -nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{V_i}{V_f} = nRT \ln \frac{P_f}{P_i}$$

If we remember the Boyle’s law $P_iV_i = P_fV_f$. 
Work of expansion (7)

As the general expression for work of expansion is: \( dw = -PdV \)

and after integration:

\[
\int_{i}^{f} dw = -\int_{i}^{f} P(V) dV
\]

hence, work is represented by the surface area under the \( P=f(V) \) plot on the P-V plane.

It is also clearly visible that work is not a state property, as transition from state 1 to state 2, produces different work, depending on the path (A or B).
**Polytropic processes**

General form of equation: \( PV^x = \text{const} \) describes different processes, depending on the value of \( x \).

<table>
<thead>
<tr>
<th>value of ( x )</th>
<th>process described</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>isobaric</td>
</tr>
<tr>
<td>1</td>
<td>isothermal</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>adiabatic</td>
</tr>
<tr>
<td>( \infty )</td>
<td>isochoric</td>
</tr>
</tbody>
</table>

The higher the exponent \( X \), the steeper is the curve on the P-V plane (from horizontal – isobaric), through hyperboles to vertical straight line (isovolumic).
**Kirchoff’s law**

How to calculate heat of reaction at different temperature?

![Diagram of heat of reaction at different temperatures](image)

- **Reactants at T<sub>1</sub>** with **ΔH<sub>Heat. react.</sub>**
- **Reactants at T<sub>2</sub>** with **ΔH<sub>r,T1</sub>**
- **Product at T<sub>1</sub>** with **ΔH<sub>r,T1</sub>**
- **Product at T<sub>2</sub>** with **ΔH<sub>cool. prod.</sub>**

**T<sub>2</sub> > T<sub>1</sub>**

Please, devote some attention to the diagram shown. Similar approach will enable us to solve many problems.

Strictly speaking, the scheme does not represent a cycle (it is a direct process and a bypass, or detour, both leading, though, from the same initial to the same final state). What is a cycle? Try to define.

It is assumed here that T<sub>2</sub> > T<sub>1</sub>, but it works perfectly also for T<sub>1</sub> > T<sub>2</sub>. 
Kirchoff’s law (2)

Enthalpy is a state function, hence:

\[ \Delta H = \Delta H_{\text{heat.react.}} + \Delta H_{\text{cool.prod.}} \]

\[ \Delta H_2 = \Delta H_1 - \Delta H_{\text{heat.react.}} - \Delta H_{\text{cool.prod.}} \]

\[ \Delta H_2 = \Delta H_1 - \int_{T_1}^{T_2} C_{P,\text{re}} \, dT - \int_{T_1}^{T_2} C_{P,pr} \, dT = \Delta H_1 + \int_{T_1}^{T_2} C_{P,pr} \, dT - \int_{T_1}^{T_2} C_{P,\text{re}} \, dT \]

\[ \Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_P(T) \, dT \]
Kirchoff’s law (3)

\[ \Delta H_2 = \Delta H_1 + \int_{T_i}^{T_2} \Delta C_p(T)\,dT \]

\[
\Delta C_p = \sum n_i C_{p,i,pr} - \sum n_i C_{p,i,re}
\]

For a reaction expressed as: \( aA + bB + \ldots = lL + mM + \ldots \)

\[
\Delta C_{p,r} = lC_{pL} + mC_{pM} + \ldots - aC_{pA} - bC_{pB} - \ldots = \left( \frac{\partial (\Delta H_r)}{\partial T} \right)_p
\]
**Kirchoff’s law (4)**

When: \[ C_p \neq f (T); \quad C_p = \text{const} \]

the general formula: \[ \Delta H_2 = \Delta H_1 + \int_{T_i}^{T_f} \Delta C_p (T') dT \]

may be simplified to: \[ \Delta H_2 = \Delta H_1 + \int_{T_i}^{T_f} \Delta C_p dT \]

and finally to: \[ \Delta H_2 = \Delta H_1 + \Delta C_p \Delta T \]

Kirchoff’s law may be applied to internal energy of reactions, \( \Delta U_r \), (they are state functions, too) using \( C_V \) instead of \( C_p \).
Enthalpy and internal energy of a reaction

First principle of thermodynamics says: $\Delta U = q + w$

For an isobaric process: $q = \Delta H$, $w = -P \Delta V$

Therefore: $\Delta U = \Delta H - P \Delta V$

The same must be true, when a chemical reaction occurs in the system

$$\Delta U_r = \Delta H_r - P \Delta V = \Delta H_r - \Delta n_g RT$$

Because: $\Delta V = \frac{\Delta n_g RT}{P}$, $\Delta n_g = n_{g, pr} - n_{g, re}$

Subscript $g$ in $n_g$ and $\Delta n_g$ means that what counts are gas phase (gaseous) products and reactants.

For liquid phase reactions, not to say the solid state reactions, differences between enthalpy of reaction and internal energy of reaction are much smaller.