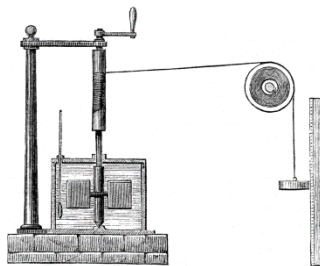


1. In the attempt to measure the heat equivalent of mechanical work (as Joule did in his famous experiment) a student uses an apparatus similar to that shown below:



The 1.50 kg weight is lifted 30.0 cm against the force due to gravity (9.8 N). If the specific heat of water is $4.184 \frac{J}{g^{\circ}C}$, what is the expected temperature increase of the 1.5 kg of water in the canister?

$$w = F \cdot \Delta x$$

$$w = 9.8 \text{ N} \cdot 30.0 \text{ cm} \cdot \frac{m}{100 \text{ cm}} \cdot \frac{J}{N \cdot m} = 2.94 \text{ J} = q$$

$$q = mC\Delta T$$

$$2.94 \text{ J} = (1500 \text{ g}) \left(4.184 \frac{J}{g^{\circ}C} \right) \Delta T$$

$$\Delta T = 0.000468^{\circ}C$$

2. 1.00 mol of an ideal gas, initially occupying 12.2 L at 298 K, expands isothermally against a constant external pressure of 1.00 atm until the pressure of the gas is equal to the external pressure. Calculate Δp , q , w , ΔU , and ΔH for the expansion.

The change in pressure calculation requires the use of the ideal gas law to determine the initial pressure:'

$$\begin{aligned} \Delta p &= p_f - p_i \\ &= 1.00 \text{ atm} - \frac{(1.00 \text{ mol}) \left(0.08206 \frac{\text{atm L}}{\text{mol K}} \right) (298 \text{ K})}{12.2 \text{ L}} \\ &= -1.0044 \text{ atm} \end{aligned}$$

The work is given by

$$w = -p_{\text{ext}}\Delta V$$

$$\begin{aligned}
 &= -(1.00 \text{ atm}) \left[\frac{\left((1.00 \text{ mol}) \left(0.08206 \frac{\text{atm L}}{\text{mol K}} \right) (298 \text{ K}) \right)}{1.00 \text{ atm}} - 12.2 \text{ L} \right] \left(\frac{8.314 \text{ J}}{0.08206 \text{ atm L}} \right) \\
 &= -1241.5 \text{ J}
 \end{aligned}$$

Because the process is isothermal, ΔU and ΔH are both zero. And because ΔU is zero, $q = -w$. So

$$\begin{aligned}
 \Delta U &= 0 \\
 \Delta H &= 0 \\
 q &= 1241.5 \text{ J}
 \end{aligned}$$

3. Consider 1.00 mol of an ideal gas expanding isothermally at 298 K from an initial volume of 12.2 L to a final volume of 22.4 L. Calculate Δp , q , w , ΔU , and ΔH for the expansion.

First, the change in pressure:

$$\begin{aligned}
 \Delta p &= p_f - p_i \\
 &= (1.00 \text{ mol}) \left(0.08206 \frac{\text{atm L}}{\text{mol K}} \right) (298 \text{ K}) \left(\frac{1}{22.4 \text{ L}} - \frac{1}{12.2 \text{ L}} \right) \\
 &= -0.913 \text{ atm}
 \end{aligned}$$

For an isothermal change

$$\Delta U = \Delta H = 0$$

For an isothermal, reversible expansion of an ideal gas

$$\begin{aligned}
 w &= -nRT \ln \left(\frac{V_f}{V_i} \right) \\
 &= -(1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (298 \text{ K}) \ln \left(\frac{22.4 \text{ L}}{12.2 \text{ L}} \right) \\
 &= -1505.4 \text{ J}
 \end{aligned}$$

And since $\Delta U = 0$, $q = -w$.

$$q = 1505.4 \text{ J}$$

4. Consider 1.00 mol of an ideal gas ($C_V = 3/2 R$) occupying 22.4 L that undergoes an isochoric (constant volume) temperature increase from 298 K to 342 K. Calculate Δp , q , w , ΔU , and ΔH for the change.

For an isochoric change, $\Delta V = 0$. So,

$$w = 0$$

Then, we can get q and ΔU from

$$\begin{aligned} q = \Delta U &= nC_V\Delta T \\ &= (1.00 \text{ mol}) \left(\frac{3}{2} \cdot 8.314 \frac{\text{J}}{\text{mol K}} \right) (342 \text{ K} - 298 \text{ K}) \\ &= 548.724 \text{ J} = 549 \text{ J} \end{aligned}$$

And to get ΔH ,

$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) = \Delta U + nR\Delta T \\ &= 548.7 \text{ J} + (1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (342 \text{ K} - 298 \text{ K}) \\ &= 914.52 \text{ J} = 915 \text{ J} \end{aligned}$$

5. Consider 1.00 mol of an ideal gas ($C_p = 5/2 R$) initially at 1.00 atm that undergoes an isobaric expansion from 12.2 L to 22.4 L. Calculate ΔT , q, w, ΔU , and ΔH for the change.

First, let's find ΔT . To do this, we can use the ideal gas law! According to the ideal gas law,

$$T = \frac{pV}{nR}$$

So

$$\begin{aligned} \Delta T &= T_2 - T_1 = \frac{p}{nR} (V_2 - V_1) \\ &= \frac{1.00 \text{ atm}}{(1.00 \text{ mol}) \left(0.08206 \frac{\text{atm L}}{\text{mol K}} \right)} (22.4 \text{ L} - 12.2 \text{ L}) \\ &= 124.3 \text{ K} \end{aligned}$$

For an isobaric ($\Delta p = 0$) change,

$$\begin{aligned} q = \Delta H &= nC_p\Delta T \\ &= (1.00 \text{ mol}) \left(\frac{5}{2} \cdot 8.314 \frac{\text{J}}{\text{mol K}} \right) (123.4 \text{ K}) \\ &= 2564.9 \text{ J} = 2560 \text{ J} \end{aligned}$$

To get ΔU , we can use

$$\begin{aligned}
 \Delta U &= \Delta H - \Delta(pV) = \Delta H - nR\Delta T \\
 &= 2564.9 J - (1.00 \text{ mol}) \left(8.314 \frac{J}{\text{mol K}} \right) (124.3 K) \\
 &= 1531.47 J = 1530 J
 \end{aligned}$$

And finally, to find w

$$\begin{aligned}
 w &= \Delta U - q = 1531.47 J - 2564.9 J \\
 &= -1033.43 J = -1030 J
 \end{aligned}$$

6. Consider 1.00 mol of an ideal gas ($C_V = 3/2 R$) initially at 12.2 L and 1.00 atm that undergoes an adiabatic expansion to 22.4 L. Calculate ΔT , q, w, ΔU , and ΔH for the change.

For an adiabatic change,

$$q = 0$$

Now that that is out of the way, the first thing to calculate will be the final temperature. Well, actually, the first thing to do is to find the initial temperature.

$$\begin{aligned}
 T &= \frac{pV}{nR} \\
 &= \frac{(1.00 \text{ atm})(12.2 \text{ L})}{(1.00 \text{ mol}) \left(0.08206 \frac{\text{atm L}}{\text{mol K}} \right)} \\
 &= 148.67 K
 \end{aligned}$$

Now, to get the final temperature, we can use the relationship

$$\begin{aligned}
 V_1 T_1^{\frac{C_V}{R}} &= V_2 T_2^{\frac{C_V}{R}} \\
 (12.2 \text{ L})(148.67 K)^{\frac{3}{2}} &= (22.4 \text{ L})(T_2)^{\frac{3}{2}} \\
 T_2 &= 99.15 K
 \end{aligned}$$

So ΔT is

$$\begin{aligned}
 \Delta T &= T_2 - T_1 \\
 &= 99.15 K - 148.67 K
 \end{aligned}$$

$$= -49.52 \text{ K} = -50 \text{ K}$$

Now, let's find w and ΔU .

$$\begin{aligned} w = \Delta U &= nC_V \Delta T \\ &= (1.00 \text{ mol}) \left(\frac{3}{2} \cdot 8,314 \frac{\text{J}}{\text{mol K}} \right) (-49.52 \text{ K}) \\ &= -617.6 \text{ J} = -620 \text{ J} \end{aligned}$$

And ΔH can be determined by

$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) = \Delta U + nR\Delta T \\ &= -617.6 \text{ J} + (1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (-49.52 \text{ K}) \\ &= -1029.3 \text{ J} = -1030 \text{ J} \end{aligned}$$

7. Derive an expression for the work of an isothermal, reversible expansion of a gas that follows the equation of state (in which a is a parameter of the gas)

$$pV = nRT - \frac{an^2}{V}$$

from V_1 to V_2 .

Work for a reversible change is calculated from

$$dw = -p dV$$

And from the equation of state, we can solve for p .

$$p = \frac{nRT}{V} - \frac{an^2}{V^2}$$

So

$$\begin{aligned} dw &= - \left(\frac{nRT}{V} - \frac{an^2}{V^2} \right) dV \\ w &= - \int_{V_1}^{V_2} \left(\frac{nRT}{V} - \frac{an^2}{V^2} \right) dV \\ w &= -nRT \int_{V_1}^{V_2} \frac{dV}{V} - an^2 \int_{V_1}^{V_2} \frac{dV}{V^2} \end{aligned}$$

$$w = -nRT \ln \left(\frac{V_2}{V_1} \right) + an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

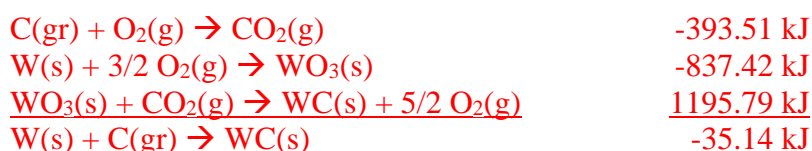
8. Use the following data [Huff, Squitieri, and Snyder, J. Am. Chem. Soc., **70**, 3380 (1948)] to calculate the standard enthalpy of formation of tungsten carbide, WC(s).

Reaction	ΔH° (kJ)
$\text{C}(\text{gr}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-393.51
$\text{WC}(\text{s}) + 5/2 \text{O}_2(\text{g}) \rightarrow \text{WO}_3(\text{s}) + \text{CO}_2(\text{g})$	-1195.79
$\text{W}(\text{s}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{WO}_3(\text{s})$	-837.42

To find the enthalpy of formation, we need to generate the formation reaction



from the data reactions. This can be accomplished by adding the first and third reactions to the reverse of the second reaction.



9. The standard molar enthalpy of combustion (ΔH_c) of propane gas is given by



The standard molar enthalpy of vaporization (ΔH_{vap}) for liquid propane



- Calculate the standard enthalpy of combustion of liquid propane.
 - Calculate the standard internal energy change of vaporization (ΔU_{vap}) for liquid propane.
 - Calculate the standard internal energy change of combustion (ΔH_c) for liquid propane.
10. The enthalpy of combustion (ΔH_c) of aluminum borohydride, $\text{Al}(\text{BH}_4)_3(\text{l})$, was measured to be -4138.4 kJ/mol [Rulon and Mason, J. Am. Chem. Soc., **73**, 5491 (1951)]. The combustion reaction for this compound is given by



Given the following additional data, calculate the enthalpy of formation of $\text{Al}(\text{BH}_4)_3(\text{g})$.

$\text{Al}_2\text{O}_3(\text{s})$	$\Delta H_f = -1669.8 \text{ kJ/mol}$
$\text{B}_2\text{O}_3(\text{s})$	$\Delta H_f = -1267.8 \text{ kJ/mol}$
$\text{H}_2\text{O}(\text{l})$	$\Delta H_f = -285.84 \text{ kJ/mol}$
$\text{Al}(\text{BH}_4)_3(\text{l})$	$\Delta H_{\text{vap}} = 30.125 \text{ kJ/mol}$

$$-4138.4 \text{ kJ} = (6 \text{ mol}) \left(-285.84 \frac{\text{kJ}}{\text{mol}} \right) + \left(\frac{3}{2} \text{ mol} \right) \left(-1267.8 \frac{\text{kJ}}{\text{mol}} \right) + \left(\frac{1}{2} \text{ mol} \right) \left(-1669.8 \frac{\text{kJ}}{\text{mol}} \right) - (1 \text{ mol}) (\Delta H_{f, \text{Al}(\text{BH}_4)_3(\text{l})})$$

$$\Delta H_{f, \text{Al}(\text{BH}_4)_3(\text{l})} = +313.24 \frac{\text{kJ}}{\text{mol}}$$

Then



$$30.125 \frac{\text{kJ}}{\text{mol}} = \Delta H_{f, \text{Al}(\text{BH}_4)_3(\text{g})} - \Delta H_{f, \text{Al}(\text{BH}_4)_3(\text{l})}$$

$$30.125 \frac{\text{kJ}}{\text{mol}} = \Delta H_{f, \text{Al}(\text{BH}_4)_3(\text{g})} - 313.24 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_{f, \text{Al}(\text{BH}_4)_3(\text{g})} = 343.365 \frac{\text{kJ}}{\text{mol}}$$

11. The standard enthalpy of formation (ΔH_f°) for water vapor is -241.82 kJ/mol at 25°C . Use the data in the following table to calculate the value at 100°C .

Substance	$C_p \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$
$\text{H}_2(\text{g})$	28.84
$\text{O}_2(\text{g})$	29.37
$\text{H}_2\text{O}(\text{g})$	33.58

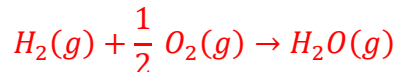
To find $\Delta H^\circ(100^\circ\text{C})$, we can use

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT$$

And if we assume that ΔC_p is independent of temperature over the temperature interval,

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p \Delta T$$

The formation reaction for $H_2O(g)$ is



So, ΔC_p can be calculated from

$$\begin{aligned}\Delta C_p &= C_{p,H_2O(g)} - C_{p,H_2(g)} - \frac{1}{2} C_{p,O_2(g)} \\ &= 33.58 \frac{J}{mol\ K} - 28.84 \frac{J}{mol\ K} - \left(\frac{1}{2}\right) 29.37 \frac{J}{mol\ K} \\ &= -9.945 \frac{J}{mol\ K}\end{aligned}$$

And $\Delta H^\circ(100\ ^\circ C)$ can be found from

$$\begin{aligned}\Delta H_{100\ ^\circ C} &= \Delta H_{25\ ^\circ C} + \Delta C_p (100\ ^\circ C - 25\ ^\circ C) \left(\frac{K}{^\circ C}\right) \\ &= -241820 \frac{J}{mol} - 9.945 \frac{J}{mol\ K} (75\ K) \\ &= -242565.9 \frac{J}{mol} = -242.57 \frac{kJ}{mol}\end{aligned}$$

12. For a reaction $2 A \rightarrow A_2$, $\Delta H_{298} = -5.00\ kJ$. The change in constant pressure heat capacity is given by

$$\Delta C_p = 1 + bT$$

where $a = 1.00\ J/K$ and $b = 2.00 \times 10^{-3}\ J/K^2$. Find the temperature at which $\Delta H = 0$.

To solve this, we need to use the temperature dependence of the reaction enthalpy

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p\ dT$$

For convenience, let's say

$$a = 1.00 \frac{J}{K} \quad \text{and} \quad b = 2.00 \cdot 10^{-3} \frac{J}{K^2}$$

So that

$$\Delta C_p = a + bT$$

The integral isn't too hard

$$\begin{aligned}\int_{T_1}^{T_2} \Delta C_p dT &= \int_{T_1}^{T_2} (a + bT) dT \\ &= a[T]_{T_1}^{T_2} + \frac{b}{2} [T^2]_{T_1}^{T_2} \\ &= a(T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2)\end{aligned}$$

Plugging this in yields

$$\Delta H_{T_2} = \Delta H_{T_1} + a(T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2)$$

And plugging in values for a and b, and setting $\Delta H_{T_2} = 0$ and $T_1 = 298 \text{ K}$:

$$0 = -5000 \text{ J} + \left(1.00 \frac{\text{J}}{\text{K}}\right) (T_2 - 298 \text{ K}) + \frac{2.00 \cdot 10^{-3} \frac{\text{J}}{\text{K}^2}}{2} [T_2^2 - (298 \text{ K})^2]$$

This quadratic equation has two roots:

$$\begin{aligned}T_2 &= -2874.2 \text{ K} \\ T_2 &= +1874.2 \text{ K}\end{aligned}$$

Clearly, we can reject the negative root. So the answer is

$$T_2 = 1870 \text{ K}$$

13. From the following data, determine the lattice energy of BaBr_2 .

$\text{Ca(s)} \rightarrow \text{Ca(g)}$	$\Delta H_{\text{sub}} = 129 \text{ kJ/mol}$
$\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$	$\Delta H_{\text{vap}} = 31 \text{ kJ/mol}$
$\text{Br}_2(\text{g}) \rightarrow 2 \text{ Br(g)}$	$D(\text{Br-Br}) = 193 \text{ kJ/mol}$
$\text{Ca(g)} \rightarrow \text{Ca}^+(\text{g}) + \text{e}^-$	$1^{\text{st}} \text{ IP(K)} = 589.8 \text{ kJ/mol}$
$\text{Ca}^+(\text{g}) \rightarrow \text{Ca}^{2+}(\text{g}) + \text{e}^-$	$2^{\text{nd}} \text{ IP(K)} = 1145.4 \text{ kJ/mol}$
$\text{Br(g)} + \text{e}^- \rightarrow \text{Br}^-(\text{g})$	$1^{\text{st}} \text{ EA(Br)} = 194 \text{ kJ/mol}$
$\text{Ca(s)} + \text{Br}_2(\text{l}) \rightarrow \text{CaBr}_2(\text{s})$	$\Delta H_{\text{f}} = -675 \text{ kJ/mol}$

14. Using average bond energies

(http://chem.libretexts.org/Reference/Reference_Tables/Thermodynamics_Tables/T3%3A_Bond_Energies) estimate the reaction enthalpy for the reaction



From the table, we find the following data:

Bond	Bond Energy (kJ/mol)
C-H	413
C-Br	276
H-Br	366
C-C	614
C=C	348

For the reaction to occur, forming 1 mole of $\text{C}_2\text{H}_5\text{Br}$, 1 mole of each of the following bonds must be broken ($\Delta H > 0$) and formed ($\Delta H < 0$)

Broken	ΔH (kJ/mol)	Formed	ΔH (kJ/mol)
C=C	348	C-C	-614
H-Br	366	C-H	-413
		C-Br	-276

Adding all of the bond enthalpies yields the estimated reaction enthalpy:

$$\Delta H_{\text{rxn}} = 1 \text{ mol} \left(348 \frac{\text{kJ}}{\text{mol}} + 366 \frac{\text{kJ}}{\text{mol}} - 614 \frac{\text{kJ}}{\text{mol}} - 413 \frac{\text{kJ}}{\text{mol}} - 276 \frac{\text{kJ}}{\text{mol}} \right) = -589 \text{ kJ}$$