

1. From the following list of variables/properties, circle all the **EXTENSIVE** variables/properties.

Density
Number of moles
Heat Capacity

Total Energy
Concentration
Volume

Temperature
Pressure
Mass

Viscosity Coefficient
Diffusion Coefficient

Volume, mass, heat capacity, number of moles, total energy.

2. A CHEM 154 student is interested in commercializing a hot pack that takes advantage of the exothermic dissolution of CaCl_2 in water. To this end, the student did a hot pack experiment and collected the data in the table to the right. Assume dissolved CaCl_2 doesn't affect the heat capacity or the mass of the solution appreciably. (For a challenge, trying solve part a) without these assumptions.)

Mass of CaCl_2	22 g
Mass of water	95 g
T_i	25 °C
T_f	66 °C

- a) How much CaCl_2 , in g, must the student dissolve to heat 30 mL of water at 5° to 30 °C? ($c_{p,\text{water}} = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$)

The mass of the solution (water and dissolved CaCl_2), m_{sol} is calculated from V_{water} assuming the density of water is equal to 1 g/mL and ignoring the mass of the dissolved CaCl_2 . The heat necessary to increase the temperature of the solution is (assuming the dissolved CaCl_2 doesn't change the heat capacity of the water appreciably)

$$q = m_{\text{sol}} c_{p,\text{water}} \Delta T = 30 \text{ g} \times 4.184 \frac{\text{J}}{\text{g K}} \times 25 \text{ K} = 3.138 \text{ kJ}$$

Using the experimental data in the table shows that 22 g of CaCl_2 produced the following amount of heat, which under the same assumptions as above gives

$$q = m_{\text{sol}} c_{p,\text{water}} (T_f - T_i) = 95 \text{ g} \times 4.184 \frac{\text{J}}{\text{g K}} \times 41 \text{ K} = 16.30 \text{ kJ}$$

so the mass required to produce 3.138 kJ is

$$\text{Unknown mass } \text{CaCl}_2 = \frac{3.138 \text{ kJ}}{16.30 \text{ kJ}} \times 22 \text{ g} = 4.24 \text{ g}$$

For the optional challenge solution to this question, let m_w and m represent masses of water and CaCl_2 , respectively. The heat calculation for part a) then gives

$$q_a = (m + m_w) c_{p,a} \Delta T = (m + 30) \times c_{p,a} \times 25 = 25(m + 30) c_{p,a}$$

in which m is the unknown mass of CaCl_2 we are seeking, and $c_{p,a}$ is the heat capacity of the resulting solution. By a similar calculation, the experimental data gives

$$q_b = (m + m_w)c_{p,b}\Delta T = (22 + 95) \times c_{p,b} \times 41 = 4797c_{p,b}$$

in which $c_{p,b}$ is the heat capacity of the resulting solution. Let ΔH be the heat released per gram of dissolved CaCl_2 , so that $q_a = m\Delta H$ and $q_b = 22\Delta H$. Equating the expressions for q_b gives

$$q_b = 22\Delta H = 4797c_{p,b} \rightarrow \Delta H = 218.0 c_{p,b}$$

which when substituted into the expression for q_a gives

$$q_a = m\Delta H = m218.0c_{p,b} = 25(m + 30)c_{p,a} \rightarrow m = \frac{25 \times 30c_{p,a}}{(218.0c_{p,b} - 25c_{p,a})}$$

Without additional information we can't proceed further unless we assume $c_{p,a} = c_{p,b}$, that is the heat capacities of the two solutions are the same. Note that this heat capacity won't have the value for pure water, and in fact we don't actually need to know the precise value of it. All we need to know is that the solutions created in the experiment and in part a) have comparable heat capacities, meaning we hope the value isn't a strong function of concentration. With that assumption, we can cancel the factors of the heat capacity and solve for the value of m giving 3.89 g (about 9% smaller than the value calculated above).

- b) Would switching the solvent from water to methanol ($c_p = 1.7 \text{ J g}^{-1} \text{ K}^{-1}$) make the hot pack work better than with water? What other factors must the CHEM 154 student consider?

Based solely on heat capacity yes. Because less CaCl_2 will be required to heat methanol by the same amount. However, there may be solubility issues (CaCl_2 may not dissolve readily in MeOH). Also, the dissolution may not be as exothermic. As a positive, the freezing temperature of methanol is -90°C so it could be used at temperatures below freezing. The point is, there are many factors to be considered.

3. A quantity of 0.850 moles of an ideal gas initially at a pressure of 15.0 atm and 300 K is allowed to expand isothermally until its final pressure is 1.00 atm. Calculate the work done, in kJ, when the expansion is done against a constant external pressure. (*Hint: Use the ideal gas law.*) Is this process reversible or irreversible? (Please explain your answer.)

$$V_i = \frac{nRT}{P_i} \quad V_f = \frac{nRT}{P_f} \quad P_{ext} = P_f = 1.00 \text{ atm}$$

$$w = -P_{ext}\Delta V = -P_{ext}(V_f - V_i) = -nRT P_f \left(\frac{1}{P_f} - \frac{1}{P_i} \right)$$

$$w = -(0.850 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(300 \text{ K})(1.00 \text{ atm}) \\ \times \left(\frac{1}{1.00 \text{ atm}} - \frac{1}{15.0 \text{ atm}} \right)$$

$$w = -19.5 \text{ L atm} \left(101.325 \frac{\text{J}}{\text{L atm}} \right) = -1.98 \text{ kJ}$$

This process is irreversible because it is a volume change induced by a finite pressure difference between the system and surroundings. The expansion proceeds spontaneously and cannot be reversed by a minor perturbation.

4. Work may be done by a system or on the system during phase changes. Calculate the work done (in J) for:
- a) The complete conversion of 1 mol of ice to water at 273 K and 1 atm. The molar volumes of ice and water at 273 K are 0.0196 L mol⁻¹ and 0.0180 L mol⁻¹, respectively.

$$w = -P\Delta V = -(1 \text{ atm})(1 \text{ mol})(0.0180 \text{ L mol}^{-1} - 0.0196 \text{ L mol}^{-1}) \\ = -(1 \text{ atm})(1 \text{ mol})(-0.0016 \text{ L mol}^{-1}) \\ = 0.0016 \text{ L atm} \left(101.325 \frac{\text{J}}{\text{L atm}} \right) = 0.162 \text{ J}$$

- b) The complete conversion of 1 mol of water to steam at 373 K and 1 atm. The molar volumes of water and steam at 373 K are 0.0188 L mol⁻¹ and 30.61 L mol⁻¹, respectively.

$$w = -P\Delta V = -(1 \text{ atm})(1 \text{ mol})(30.61 \text{ L mol}^{-1} - 0.0188 \text{ L mol}^{-1}) \\ = -(1 \text{ atm})(1 \text{ mol})(30.5912 \text{ L mol}^{-1}) \\ = -30.5912 \text{ L atm} \left(101.325 \frac{\text{J}}{\text{L atm}} \right) = -3100 \text{ J}$$

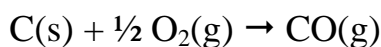
Note: $P_{ext} = P$ has already been used in the equations for a) and b) since the external pressure is constant during phase changes.

- c) Compare and contrast your answers to parts a) and b) based on chemical/physical structural changes.

Work is a positive quantity going from solid to liquid H₂O as the solid has a higher molar volume compared to the liquid. This can be explained by the fact that water expands when it freezes, and solid H₂O has a LOWER density compared to the liquid – ice floats! In this case, melting causes a contraction in the volume and represents work done on the system by the surroundings – work is a positive quantity.

For liquid to gas H₂O, the value of work is negative and is significantly larger compared to that for the melting of ice. This can be explained by the fact that the sample of H₂O significantly expands when water is vapourized. This represents work done by the system on the surroundings, leading to a negative quantity for work.

5. One mole of carbon and 0.5 mol of oxygen undergo the reaction



in an enclosed container with a freely moveable piston exposed to a constant external pressure of 1 atm and immersed in a heat bath at 298 K. The heat evolved for the reaction as written is determined to be -213.21 kJ.

- a) Determine the volume change for the reaction.

$$\Delta V = \frac{\Delta nRT}{P} = \frac{(0.5 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1 \text{ atm}} = 12.23 \text{ L}$$

- b) For the production of 1 mol of CO(g), determine the amount of work performed (in kJ). Rationalize the sign of work performed.

$$\begin{aligned} w &= -P\Delta V = -(1 \text{ atm})(12.23 \text{ L}) = (-12.23 \text{ L atm}) \left(101.325 \frac{\text{J}}{\text{L atm}} \right) \\ &= -1239 \text{ J} = -1.24 \text{ kJ} \end{aligned}$$

Work is negative as the volume of the container is expanding. Note P_{ext} has been replaced with P in the work expression since P_{ext} is constant.

- c) Using the above, determine ΔU for the reaction (in kJ).

$$\Delta U = q + w = -213.21 \text{ kJ} - 1.24 \text{ kJ} = -214.45 \text{ kJ}$$

6. **Good question.** Heat transfer is not a state function and as such it is path dependent. Consider a subliming solid “S”: $S(s) \rightarrow S(g)$ at constant temperature. This process may proceed in two ways. In one case S sublimes in a container open to the atmosphere (constant pressure). In the other case it sublimes in a stoppered flask (constant volume). Which case will result in the greater energy transfer in the form of heat? Explain your answer.

Several scenarios are possible.

Scenario 1: The amount of solid is large (enough).

In this scenario, the solid will sublime in the constant volume case until the pressure of the gas reaches the vapour pressure, at which point the system attains equilibrium. In the constant pressure case, the entire solid will sublime. Thus, more heat will flow in the latter case in order to provide the energy to sublime the entire solid.

Scenario 2: The amount of solid is small (enough).

In this scenario, the entire solid sublimes to gas in both the constant volume and constant pressure cases. The ΔU needed for this phase change is the same in both cases. However, if the gas expands into a fixed volume, no volume change occurs in the system and the work is zero. In principle, this expansion could produce a small ΔU if the gas is not ideal. In the constant pressure case, this gas expands against a constant external atmospheric pressure, so work is done by the system ($w < 0$). The energy for this work must come from the surroundings since the process is isothermal, so heat must flow into the system to provide this additional energy.

In both scenarios, greater energy is transferred as heat when pressure is constant.

7. **Good question.** Calculate the total heat, in kJ, required to change an 18.0 g ice cube initially at a temperature of $-5.00\text{ }^{\circ}\text{C}$ to water at a temperature of $75\text{ }^{\circ}\text{C}$, all at 1 atm constant pressure.

Three steps are required:

- 1. Heating of ice cube from $-5\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$**
- 2. Melting of ice cube at $0\text{ }^{\circ}\text{C}$**
- 3. Heating of liquid water to $75\text{ }^{\circ}\text{C}$**

	Specific heat ($\text{J g}^{-1} \text{K}^{-1}$)	Enthalpy of phase transition (kJ mol^{-1})
$\text{H}_2\text{O}(s)$	2.09	$\Delta H^{\circ}(\text{fus}) = 6.01$
$\text{H}_2\text{O}(l)$	4.18	$\Delta H^{\circ}(\text{vap}) = 40.6$
$\text{H}_2\text{O}(g)$	2.03	

$$q_1 = mc\Delta T = (18\text{ g})(2.09)(5) = 188\text{ J}$$

$$q_2 = n\Delta H = \frac{(18\text{ g})}{(18\text{ g mol}^{-1})} \left(6.01 \frac{\text{kJ}}{\text{mol}} \right) = 6.01\text{ kJ} = 6010\text{ J}$$

$$q_3 = mc\Delta T = (18\text{ g})(4.18\text{ J g}^{-1} \text{K}^{-1})(75\text{ K}) = 5643\text{ J}$$

$$q_{\text{total}} = q_1 + q_2 + q_3 = 188\text{ J} + 6010\text{ J} + 5643\text{ J} = 11841\text{ J} = 11.8\text{ kJ}$$

8. **Good question.** 981.0 kJ of heat are released when 1 mol of glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) undergoes a combustion reaction at constant atmospheric pressure (1 atm). Calculate q , w , ΔU and ΔH when 5.0 g of glycine are burned at a constant pressure of 1.00 atm and $T = 298 \text{ K}$. Assume the combustion products are carbon dioxide gas, nitrogen gas, and liquid water. Molar mass of glycine = 75.07 g mol^{-1} . (Hint: Write out the combustion reaction for one mole of glycine.)



$$q_P = \Delta H_{\text{combustion}} = -981.0 \text{ kJ mol}^{-1} \times \left(\frac{5 \text{ g}}{75 \text{ g mol}^{-1}} \right) = -65.4 \text{ kJ}$$

Note: ΔH is negative since all combustion reactions are exothermic. This is the enthalpy change/heat flow for 5 g of glycine. Since P and T are constant, the work is

$$w = -P\Delta V = -\Delta n_{\text{gas}}RT$$

Assume only gas molecules will contribute to volume change. Determine the number of moles of gas molecules on both reactants and products side, based on stoichiometric coefficients from the balanced equation. **NOTE:** Water is NOT included since it is in the liquid form.

$$\Delta n_{\text{gas}} = n_{\text{products}} - n_{\text{reactants}} = \left(2 + \frac{1}{2} \right) - \left(\frac{9}{4} \right) = \frac{5}{2} \text{ moles} - \frac{9}{4} \text{ moles} = \frac{1}{4} \text{ moles}$$

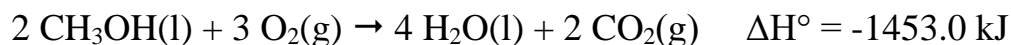
$$w = -\Delta n_{\text{gas}}RT = -\left(\frac{1}{4} \text{ moles} \right) (8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = -619 \text{ J}$$

This value of work would be for 1 mole of glycine being combusted. Must correct for the fact we only combusted 5 g of glycine.

$$w = -619 \text{ J} \times \left(\frac{5 \text{ g}}{75 \text{ g mol}^{-1}} \right) = -41.3 \text{ J} = -0.0413 \text{ kJ}$$

$$\Delta U = q_P + w = -65.4 \text{ kJ} - 0.0413 \text{ kJ} = -65.4 \text{ kJ}$$

9. Consider the combustion of methanol:



What is the value of ΔH° under each of the following conditions:

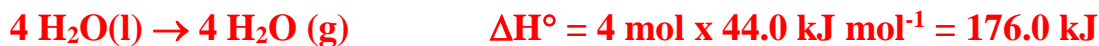
- a) 3 moles of methanol are reacted:

$$\Delta H^\circ = 1.5 \times -1453.0 \text{ kJ} = -2179.5 \text{ kJ}$$

b) The direction of the reaction is reversed:

$$\Delta H^\circ = -1 \times -1458.8 \text{ kJ} = 1453.0 \text{ kJ}$$

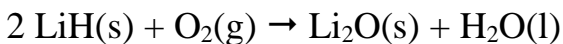
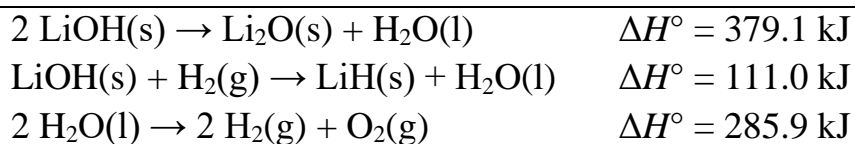
c) Water vapor is produced during the reaction instead of liquid water: ($\Delta H^\circ_{\text{vap}} = 44.0 \text{ kJ mol}^{-1}$)



Adding this equation to the one above changes the phase of water from (l) to (g), so

$$\Delta H^\circ = -1453.0 \text{ kJ} + 176.0 \text{ kJ} = -1277.0 \text{ kJ}$$

10. Lithium oxide is used to lower the melting point of ceramic precursors. Use the enthalpies at right to determine ΔH° for the reaction:



This combination can be achieved by using the reactions in this manner:

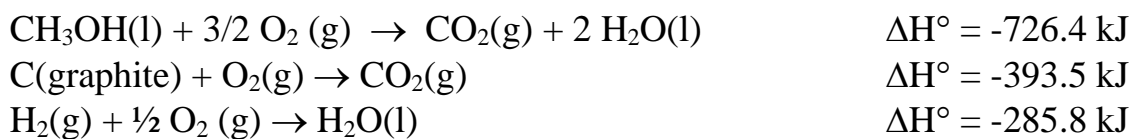
Use reaction 1 as-is (ΔH_1°)

Use reaction 2 twice and in reverse ($-2 \Delta H_2^\circ$)

Use reaction 3 in reverse ($-\Delta H_3^\circ$), so that overall

$$\Delta H^\circ = \Delta H_1^\circ - 2\Delta H_2^\circ - \Delta H_3^\circ = 379.1 \text{ kJ} + 2(-111) \text{ kJ} - 285.9 \text{ kJ} = -128.8 \text{ kJ}$$

11. **Good question.** Use the following heat of combustion data to determine the enthalpy of formation of methanol (CH_3OH).



The formation equation for methanol is from all elements in their standard state:



This combination can be achieved by:

Reverse reaction 1 ($-\Delta H_1^\circ$)

Use reaction 2 as-is (ΔH_2°)

Use reaction 3 twice ($2\Delta H_3^\circ$), so that overall

$$\Delta H_f^\circ = -\Delta H_1^\circ + \Delta H_2^\circ + 2 \Delta H_3^\circ = 726.4 - 393.5 - 571.6 = -238.7 \text{ kJ mol}^{-1}$$

12. $\Delta H_{\text{vap}}^\circ$ for the evaporation of liquid oxygen: $\text{O}_2(\text{l}) \rightarrow \text{O}_2(\text{g})$ is 6.82 kJ mol^{-1} . Determine ΔH_f° for $\text{O}_2(\text{l})$.

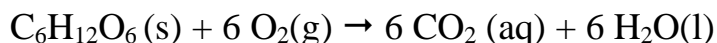
$$\Delta H_f^\circ \text{ for } \text{O}_{2(\text{g})} = 0 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vap}}^\circ = \Delta H_f^\circ(\text{O}_{2(\text{g})}) - \Delta H_f^\circ(\text{O}_{2(\text{l})})$$

$$\text{Therefore, } \Delta H_f^\circ(\text{O}_{2(\text{l})}) = \Delta H_f^\circ(\text{O}_{2(\text{g})}) - \Delta H_{\text{vap}}^\circ = 0 - 6.82 \text{ kJ mol}^{-1} = -6.82 \text{ kJ mol}^{-1}$$

13. Use the enthalpy data at right (given at 298 K) to determine the standard internal energy change (ΔU°) for the combustion of 1 mol of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) under constant pressure conditions and at 298 K:

Species	ΔH_f° (kJ/mol)
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1273.3
$\text{CO}_2(\text{aq})$	-412.9
$\text{H}_2\text{O}(\text{l})$	-285.8



$$\begin{aligned} \Delta H^\circ &= [6 \text{ mol} \times (-412.9 \text{ kJ mol}^{-1}) + 6 \text{ mol} \times (-285.8 \text{ kJ mol}^{-1})] \\ &\quad - [1 \text{ mol} \times (-1273.3 \text{ kJ mol}^{-1}) + 6 \text{ mol} \times (0 \text{ kJ mol}^{-1})] \\ &= -2918.9 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - P\Delta V = \Delta H^\circ - \Delta nRT \text{ (since } P \text{ is constant and gas treated ideally)} \\ &= -2918.9 \text{ kJ} - (-6 \text{ mol}) \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298 \text{ K}) \\ &= -2918.9 \text{ kJ} + 14.9 \text{ kJ} = -2904.0 \text{ kJ} \end{aligned}$$

14. In its standard state, elemental sulphur (rhombic) combusts to produce gaseous SO_3 . This reaction was performed with excess sulphur in a closed container with thin, flexible walls that was submerged in 3.00 L of water at 20.0°C with a constant external pressure of 1.00 bar. After the reaction, the temperature of the water increased by 2.1°C , and from the change in water height, the work was calculated as 80.0 J. Calculate: i) the mass of oxygen, in g, that reacted, ii) ΔU , in kJ, for the reaction, and iii) the standard enthalpy of formation for $\text{SO}_3(\text{g})$, in kJ/mol. ($c_{p,\text{water}} = 4.184 \text{ J/(g } ^\circ\text{C)}$)

The combustion reaction is



and since sulphur is in excess, all the oxygen is consumed in the reaction. Let n be the number of moles of oxygen consumed, thus producing $2n/3$ moles of SO_3 . The reaction happens under constant pressure, so the work is given by (treating all gases as ideal)

$$w = -P\Delta V = -R(n_2T_2 - n_1T_1) = -R\left(\frac{2}{3}nT_2 - nT_1\right)$$

Substituting in the values for work and temperatures then gives (recognizing that the work must be positive since the volume of the system decreases during the reaction)

$$80.0 \text{ J} = -8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times n \left(\frac{2}{3} \times 295.25 \text{ K} - 293.15 \text{ K} \right) \rightarrow n = 0.09990 \text{ mol}$$

The mass of reacted oxygen is then $m = 0.09990 \text{ mol} \times 32 \frac{\text{g}}{\text{mol}} = 3.20 \text{ g}$.

Because the reaction is done at a constant pressure of 1 bar, the heat released is the enthalpy change for the reaction, that is (the heat released from the reaction is the negative of the heat gained by the surrounding water)

$$\Delta H^\circ = q_P = -m_w c_w \Delta T = -3000 \text{ g} \times 4.184 \frac{\text{J}}{\text{g K}} \times 2.1 \text{ K} = -26.36 \text{ kJ}$$

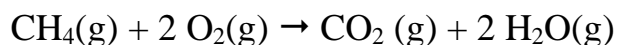
Since sulphur and oxygen are in their standard states, the standard enthalpy for the reaction is just the heat of formation for $\text{SO}_3(\text{g})$, that is (remembering that $2/3n$ moles of SO_3 are produced)

$$\Delta H^\circ = \frac{2}{3}n \Delta H_f^\circ \rightarrow \Delta H_f^\circ = -26.36 \text{ kJ} \times 1.5 \div 0.09990 \text{ mol} = -395.8 \text{ kJ mol}^{-1}$$

Finally, the change in internal energy can be calculated using the values above for work and heat, namely

$$\Delta U = q_P + w = -26.36 \text{ kJ} + 0.0800 \text{ kJ} = -26.28 \text{ kJ}$$

15. Calculate the enthalpy of combustion for methane at 1 bar of pressure using bond enthalpies.



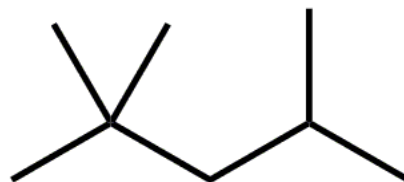
Bonds broken: 4 C-H, 2 O=O

Bonds formed: 2 C=O, 4 O-H

Consulting the bond enthalpies in the CHEM 154 Equation and Data sheet then gives

$$\begin{aligned}\Delta H^\circ &= [4 \text{ mol} \times (413 \text{ kJ mol}^{-1}) + 2 \text{ mol} \times (495 \text{ kJ mol}^{-1})] \\ &\quad - [2 \text{ mol} \times (745 \text{ kJ mol}^{-1}) + 4 \text{ mol} \times (467 \text{ kJ mol}^{-1})] \\ &= -716 \text{ kJ}\end{aligned}$$

16. **Good question.** Use bond enthalpies to estimate the energy released during the combustion of 1 mole of pure isooctane (line structure shown below). Research the importance of isooctane in the energy sector (specifically related to fuels) and briefly describe why knowledge of its enthalpy of combustion may be important.



Isooctane: $\text{C}_8\text{H}_{18} + 12.5 \text{O}_2 \rightarrow 8 \text{CO}_2 + 9 \text{H}_2\text{O}$

Bonds broken: 18 C-H bonds, 7 C-C bonds, 12.5 O=O bonds

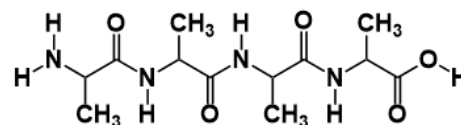
Bonds formed: 16 C=O bonds, 18 O-H bonds

Consulting the bond enthalpies in the CHEM 154 Equation and Data sheet then gives

$$\begin{aligned}\Delta H^\circ &= [18 \text{ mol} \times (413 \text{ kJ mol}^{-1}) + 7 \text{ mol} \times (347 \text{ kJ mol}^{-1}) + 12.5 \text{ mol} \\ &\quad \times (495 \text{ kJ mol}^{-1})] \\ &\quad - [16 \text{ mol} \times (745 \text{ kJ mol}^{-1}) + 18 \text{ mol} \times (467 \text{ kJ mol}^{-1})] = -4276 \text{ kJ}\end{aligned}$$

Isooctane is a gasoline additive used to reduce “engine knocking” (engine knocking can occur when compressive heating prematurely ignites the fuel air mixture). It is important to know isooctane’s enthalpy of combustion as it will affect the total energy available (and thus the mileage of the car) when the gasoline mixture is combusted.

17. **Good question.** Using bond enthalpies, estimate the enthalpy change (in kJ) released when one mole of the oligomer (short chain polymer) at right is formed from its corresponding monomers.



Note: you only need to explicitly deal with the bonds that are actually broken or formed in the condensation reaction, since the other bonds remain unchanged.

Bonds broken: 3 C-O bonds, 3 N-H bonds (assuming an acid monomer)

Bonds formed: 3 N-C bonds, 3 O-H bonds (since water is formed)

Consulting the bond enthalpies in the CHEM 154 Equation and Data sheet then gives

$$\Delta H = 3 \text{ mol} \times 358 \text{ kJ mol}^{-1} + 3 \text{ mol} \times 391 \text{ kJ mol}^{-1} - (3 \text{ mol} \times 467 \text{ kJ mol}^{-1} + 3 \text{ mol} \times 305 \text{ kJ mol}^{-1}) = -69 \text{ kJ}$$

18. An operator in a hot-air balloon activates a burner and the balloon gains altitude. Briefly describe the thermodynamics of this event in a qualitative way, identifying any heat or work done (and their signs), as well as any processes (be sure to state whether a process was done reversibly or irreversibly). If you wish and find it necessary, you may use reasonable, simplifying assumptions provided they are clearly stated.

There are many different answers for this question depending upon how one defines the system and surroundings. However, some commonalities are listed below:

- The chemical reaction in the burner is exothermic and irreversible, producing both heat and gas.**
- The balloon is flexible so processes involving it are isobaric.**
- Gravitational work is done by the system (negative) when the balloon rises. This is likely close to reversible since the balloon is always balanced against gravity and it probably gains altitude rather slowly (without causing much resulting friction in the atmosphere).**
- Heat flows (positive) from the burner to the air in the balloon, and eventually flows out (negative) of the balloon into the surrounding atmosphere (assuming the surrounding atmosphere is at a lower temperature than the balloon). These processes are all irreversible because the heat flow occurs across a finite temperature difference.**
- The balloon probably expands after the burner activates meaning it does PV-work on the surroundings (negative). This expansion is likely close to reversible since the system and surroundings are at the same pressure.**