Sample quiz and test questions - Chapter 2.
I. Terms and short answers

1. A system that can exchange neither matter nor energy with its surroundings is called

## isolated

2. A process that releases heat into the surroundings is called

## exothermic

3. Work needed to raise a mass $m$ through a height $h$ on the surface of the Earth is given by equation

$$
w=m g h
$$

4. Work of isothermal compression of an ideal gas can be calculated using the equation

$$
w=-n R T \ln \left(V_{f} / V_{i}\right)
$$

5. A reversible process is defined as

A process that can be reversed by an infinitesimal change in a parameter
6. The internal energy is

The sum of all kinetic, potential, rotational, vibrational, and electronic energy of all the atoms, ions, and molecules in the system
II. Sketch the enthalpy change diagram for the following processes and reactions:

1. $\mathrm{CO}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~s})$

$$
\Delta_{\mathrm{dep}} \mathrm{H}^{\mathrm{o}}=-33.56 \mathrm{~kJ}
$$

2. $\mathrm{C}(\mathrm{gr})+2 \mathrm{~S}(\mathrm{~s}) \rightarrow \mathrm{CS}_{2}(\mathrm{l})$
$\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}=88 \mathrm{~kJ}$

III. Calculations of $\Delta \mathrm{H}, \Delta \mathrm{U}, \mathrm{q}$, and w.

Calculate the quantities $\Delta \mathrm{H}, \Delta \mathrm{U}, \mathrm{q}$, and w for the following processes. Be sure to give signs! Gases may be considered ideal, and the volumes of liquids and solids (but not gases) may be ignored. Thermodynamic data are in Appendix A1.2.
initial state final state
(1) $0.3 \mathrm{~N}_{2}(\mathrm{~g}), 300 \mathrm{~K}, 1$ bar $\quad \rightarrow \quad 0.3 \mathrm{~N}_{2}(\mathrm{~g}), 300 \mathrm{~K}, 0.1$ bar
if this expansion occurs against a constant external pressure of 0.05 bar.
$w=-p_{\text {ext }}{ }^{*} \Delta V \quad V_{i}=0.0075 \mathrm{~m}^{3} \quad V_{f}=0.075 \mathrm{~m}^{3}$
$w=-\left(.05 * 10^{\wedge} 5\right) * 0.067=-340 \mathrm{~J} \quad q=\Delta \mathrm{U}-\mathbf{w}=+340 \mathrm{~J}$
$\Delta \mathbf{U}=\mathbf{0}$ (isothermal, ideal gas; $\mathbf{U}$ for an ideal gas depends only on $T$ )
$\Delta \mathbf{H}=\Delta \mathbf{U}+\Delta(\mathbf{p V}) ; \quad \mathbf{p V}=\mathbf{n R T}$ (ideal gas);
$\Delta(\mathrm{pV})=\mathrm{nR}(\Delta \mathrm{T})=\mathbf{0}$ (isothermal, ideal gas) $\quad \Delta \mathbf{H}=\Delta \mathbf{U}=0$
initial state
final state
(2) $0.3 \mathrm{~N}_{2}(\mathrm{~g}), 300 \mathrm{~K}, 1$ bar $\quad \rightarrow \quad 0.3 \mathrm{~N}_{2}(\mathrm{~g}), 300 \mathrm{~K}, 0.1$ bar
if this expansion occurs reversibly, with $\mathrm{p}_{\mathrm{ext}}=\mathrm{p}_{\mathrm{gas}}$.
$\mathrm{w}=-\mathrm{nRT} \ln \left(\mathbf{V}_{\mathbf{f}} / \mathbf{V}_{\mathbf{i}}\right) \quad($ see p .45$)$
$\mathbf{w}=-1720 \mathrm{~J} \quad \mathrm{q}=\Delta \mathrm{U}-\mathbf{w}=+\mathbf{1 7 2 0} \mathrm{J} ; \quad \Delta \mathrm{U}=\mathbf{0} \quad$ (isothermal, ideal gas)
$\Delta \mathbf{H}=\Delta \mathbf{U}+\Delta(\mathbf{p V})=\mathbf{0} \quad$ (isothermal, ideal gas)
initial state
final state
(3) $0.3 \mathrm{~N}_{2}(\mathrm{~g}), 300 \mathrm{~K}, 1$ bar $\quad \rightarrow \quad 0.3 \mathrm{~N}_{2}(\mathrm{~g}), 300 \mathrm{~K}, 0.0$ bar expansion into a vacuum, $\mathrm{p}_{\mathrm{ext}}=0$.
$\mathbf{w}=\mathbf{0}, \quad \mathbf{q}=\mathbf{0}, \quad \Delta \mathbf{U}=\mathbf{0}, \quad \Delta \mathbf{H}=\mathbf{0}$
initial state
$1 \mathrm{~g} \mathrm{Au}(\mathrm{s}), 273 \mathrm{~K}, 1$ bar $\quad \rightarrow \quad 1 \mathrm{~g} \mathrm{Au}(\mathrm{s}), 373 \mathrm{~K}, 1$ bar
with $\mathrm{pext}=1$ bar.
$w=-p_{\text {ext }} \Delta V=0 ; \quad$ (no gases involved, volume changes are negligible)
$\Delta H=\mathrm{q}_{\mathrm{p}}=\mathrm{n}^{*} \mathrm{C}_{\mathrm{p}, \mathrm{m}} *(\Delta \mathrm{~T})=(1 / 197) * 25.42 * 100=12.9 \mathrm{~J}$
$\mathrm{C}_{\mathrm{p}, \mathrm{m}}=25.42{\mathrm{~J}-\mathrm{mol}^{-1}-\mathrm{K}^{-1} \quad \text { (Appendix A1.2) }}^{\text {(Ap }}$
$\Delta \mathbf{U}=\Delta \mathbf{H}-\Delta(\mathbf{p V})=\Delta \mathbf{H}=12.9 \mathbf{J} \quad$ (ignore volume changes)
(5)

| initial state | final state |
| :--- | :--- | :--- |
| $\mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$ |  |$\quad \rightarrow \quad \mathrm{CaCO}_{3}(\mathrm{~s}) \mathrm{l}$

with all reactants and products at $298 \mathrm{~K}, 1$ bar.

$$
\begin{aligned}
& \Delta \mathbf{H}^{\circ}=\Delta_{\mathbf{f}} \mathrm{H}^{\circ}\left(\mathrm{CaCO}_{3}(\mathrm{~s})\right)-\Delta_{\mathrm{f}} \mathrm{H}^{\circ}(\mathbf{C a O}(\mathrm{s}))-\Delta_{\mathbf{f}} \mathbf{H}^{\circ}\left(\mathbf{C O}_{2}(\mathrm{~g})\right) \\
& \Delta \mathbf{H}^{\circ}=(-1206.9)-(-635.1)-(-393.5)=-178.3 \mathrm{~kJ} \quad \Delta \mathrm{H}^{\circ}=\mathrm{q}_{\mathrm{p}}=-178.3 \mathrm{~kJ} \\
& w=-p_{\text {ext }} \Delta V=-\left(1.00 * 10^{5} \mathrm{~Pa}\right) *\left(-\mathrm{n} * \mathrm{R} * \mathrm{~T} / \mathrm{p}_{\text {gas }}\right)=+2480 \mathrm{~J} \quad(\text { neg } \Delta \mathrm{V} \text { gives pos } \mathbf{w}) \\
& \Delta \mathrm{U}=\mathrm{q}+\mathrm{w}=\mathbf{- 1 7 8 . 3}+\mathbf{2 . 5}=\mathbf{- 1 7 5 . 8} \mathrm{kJ}
\end{aligned}
$$

initial state

final state
(6) $10 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}$, solid, $250 \mathrm{~K}, 1$ bar $\quad \rightarrow \quad 10 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}$, liquid, $350 \mathrm{~K}, 1$ bar

$$
\begin{array}{lll}
\Delta \mathrm{H}_{1} & \Delta \mathrm{H}_{2} & \Delta \mathrm{H}_{3}
\end{array}
$$

3 steps: (solid at $250 \mathrm{~K} \rightarrow$ solid at $273 \mathrm{~K} \rightarrow$ liquid at $273 \mathrm{~K} \rightarrow$ liquid at 350 K )

$$
\begin{array}{ll}
\Delta \mathbf{H}_{1}=\mathrm{n} * \mathrm{C}_{\mathrm{p}, \mathrm{~m}}\left(\mathrm{H}_{2} \mathbf{0}(\mathrm{~s})\right) * \Delta \mathrm{~T}=(10 / 18) * 37 *(273-250)=+473 \mathrm{~J} \\
\Delta \mathbf{H}_{2}=\mathrm{n} * \mathrm{C}_{\mathrm{p}, \mathrm{~m}}\left(\mathrm{H}_{2} \mathbf{0}(\mathrm{~s})\right) * \Delta \mathrm{~T}=(10 / 18) * 6010=+3340 \mathrm{~J} & \text { (Table 2.1) } \\
\Delta \mathbf{H}_{3}=\mathrm{n} * \mathbf{C}_{\mathrm{p}, \mathrm{~m}}\left(\mathrm{H}_{2} 0(\mathrm{l})\right) * \Delta \mathrm{~T}=(10 / 18) * 75.3 *(350-273)=+3220 \mathrm{~J} & \text { (Table 2.2) } \\
\text { (Table 2.1) }
\end{array}
$$

$\Delta \mathbf{H}=\mathbf{q}=+7030 \mathrm{~kJ} \quad \Delta \mathbf{U}=\Delta \mathbf{H} \quad$ (no gases involved) $\quad \mathbf{w}=0$ (no gases involved)

## IV. Problems

1. 0.850 mol of an ideal gas initially at a pressure of 15 atm and 300 K is allowed to expand isothermally until its final pressure is 2 atm . Calculate the wotk done if the expansion is carried out against a constant external pressure of 1 atm .
$\mathrm{n}=0.85 \quad \mathrm{p}_{1}=15 \mathrm{~atm} \quad \mathrm{~T}=\mathrm{const}=300 \mathrm{~K}$
$p_{2}=2 \mathrm{~atm} \quad p_{\text {ext }}=1 \mathrm{~atm}=101325 \mathrm{~Pa}$
$\mathrm{p}_{1} \mathrm{~V}_{1}=\mathrm{nRT} \rightarrow \mathrm{V}_{1}=\mathrm{nRT} / \mathrm{p}_{1}=\mathbf{0 . 8 5 \times 0 . 0 8 2 \times 3 0 0 / 1 5 \mathrm { L } = 1 . 3 9 \mathrm { L }}$
at const temp. $p_{1} V_{1}=p_{2} V_{2} \rightarrow V_{2}=p_{1} V_{1} / p_{2}=15 \times 1.39 / 2 \mathrm{~L}=1046 \mathrm{~L}$
$w=-p_{\text {ext }} \Delta V=-101325 \mathrm{~Pa}(10.46-1.39) \times 10^{-3} \mathrm{~m}^{3}=-919 \mathrm{~J}$
2. What is the specific heat capacity of a compound that rose in temperature by $2.54^{\circ} \mathrm{C}$ when its sample of a mass 5 g was supplied with 346 J of heat.
$\mathrm{C}=\mathrm{q} /(\mathrm{m} \Delta \mathrm{T})=346 \mathrm{~J} /(5 \mathrm{~g} \times 2.54 \mathrm{~K})=27.24 \mathrm{~J} /(\mathrm{g} \mathrm{K})$
3. When 0.9862 g of benzoic acid was burned in a bomb calorimeter, the temperature rose from $21.84^{\circ} \mathrm{C}$ to $25.67^{\circ} \mathrm{C}$. What is the heat capacity of the calorimeter?
In a separate experiment a quantity of 0.4654 g of glucose was burned in the same calorimeter and the temperature rose from $21.22^{\circ} \mathrm{C}$ to $22.28^{\circ} \mathrm{C}$. Calculate the enthalpy of combustion of glucose.

## Information from the tables:

Benzoic acid: $\mathrm{C}_{6} \mathrm{H}_{5} \mathbf{C O O H}, \mathrm{M}_{\mathrm{w}}=122.13 \mathrm{~g} / \mathrm{mol}, \Delta_{\text {comb }} \mathrm{H}^{0}=-\mathbf{3 2 2 7} \mathrm{kJ} / \mathrm{mol}$
Glucose: $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}, \mathrm{M}_{\mathrm{w}}=180.16 \mathrm{~g} / \mathrm{mol}$
$\mathrm{n}($ benzoic acid $)=0.9862 \mathrm{~g} / 122.13 \mathrm{~g} / \mathrm{mol}=0.0081 \mathrm{~mol}$
heat supplied to the calorimeter $q=0.0081 \mathrm{~mol} \times 3227 \mathrm{~kJ} / \mathrm{mol}=26.06 \mathrm{~kJ}$
$\mathrm{C}=\mathrm{q} / \Delta \mathrm{T}=26.06 \mathrm{~J} /(25.67-21.84) \mathrm{K}=6.8 \mathrm{~kJ} / \mathrm{K}$
$\mathrm{n}($ glucose $)=0.4654 \mathrm{~g} / 180.16 \mathrm{~g} / \mathrm{mol}=0.0026 \mathrm{~mol}$
heat evolved by cobustion of glucose sample $q=C \Delta T=6.8 \mathrm{~kJ} / \mathrm{K} \times(22.28-21.22) \mathrm{K}=$ 7.21 kJ
$\Delta_{\text {comb }} \mathrm{H}^{0}($ glucose $)=-\mathrm{q} / \mathrm{n}=-7.21 \mathrm{~kJ} / 0.0026 \mathrm{~mol}=-2772 \mathrm{~kJ} / \mathrm{mol}$
4. From the following data, calculate the enthalpies of transformations from the more stable form to the less stable form:

1. C (graphite) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta_{\mathrm{rxn}} \mathrm{H}^{\mathrm{o}}{ }_{1}=-393.51 \mathrm{~kJ}$
2. $\mathrm{C}($ diamond $)+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta_{\mathrm{rxn}} \mathrm{H}^{\mathrm{o}}{ }_{2}=-395.41 \mathrm{~kJ}$

3-2-1: $\mathrm{C}(\mathrm{d}) \rightarrow \mathrm{C}(\mathrm{gr})$
$\Delta_{\mathrm{rxn}} \mathrm{H}_{3}=\Delta_{\mathrm{rxn}} \mathrm{H}_{2}-\Delta_{\mathrm{rxn}} \mathrm{H}_{1}=-395.41 \mathrm{~kJ}-(-393.51) \mathrm{kJ}=-1.9 \mathrm{~kJ}$
5. The enthalpies of hydrogenation of ethylene and benzene have been determined at 298 K :
$\mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g}) \quad \Delta_{\mathrm{rxn}} \mathrm{H}^{\mathrm{o}}=-132 \mathrm{~kJ}$
$\mathrm{C}_{6} \mathrm{H}_{6}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{6} \mathrm{H}_{12}(\mathrm{~g}) \quad \Delta_{\mathrm{rxn}} \mathrm{H}^{\mathrm{o}}=-246 \mathrm{~kJ}$
What would be the enthalpy of hydrogenation of benzene if it contained three isolated, unconjugated double bonds? How would you account for the difference between the calculated value based on this assumption and the measured value?

The enthalpy of hydrogenation would be -396 kJ . The difference between the measured and calculated value can be explained as follows: in hydrogenation of a double bond the resultant heat is the difference between the energy required to break $\mathrm{C}=\mathrm{C}$ bond and form two C-H bonds. This difference will be greater negative value for $\mathbf{3}$ separate double bonds than for benzene due to the delocalization energy.
6. Metabolic activity in the human body releases about $1 \times 10^{4} \mathrm{~kJ}$ of heat per day. Assuming that the body is 50 kg of water, what temperature rise would the body experience if it were an isolated system? How much water must the body eliminate as perspiration to maintain the normal body temperature $\left(98.6^{\circ} \mathrm{F}\right)$. The heat of vaporization of water may be taken as $2.41 \mathrm{~kJ} / \mathrm{g}$ and the specific heat capacity as $4.18 \mathrm{~J} / \mathrm{gK}$.

$$
\begin{aligned}
& \Delta \mathrm{H}=1 \times 10^{4} \mathrm{~kJ}=1 \times 10^{7} \mathrm{~J}=\mathrm{mC} \Delta \mathrm{~T} \rightarrow \Delta \mathrm{~T}=1 \times 10^{7} \mathrm{~J} /\left(5 \times 10^{4} \mathrm{~g} \times 4.18 \mathrm{~J} / \mathrm{gK}\right)=47.85 \mathrm{~K} \\
& \Delta \mathrm{H}=\mathrm{m} \times \Delta_{\text {vap }} \mathrm{H} \rightarrow \mathrm{~m}=1 \times 10^{4} \mathrm{~kJ} / 2.41 \mathrm{~kJ} / \mathrm{g}=4149 \mathrm{~g}=4.14 \mathrm{~kg}
\end{aligned}
$$

