There are three types of systems:

- Open: & heat + matter exchanged (we are open, earth is open)
- Closed: heat exchanged (coffee cup with lid, bomb calorimeter)
- Isolated: no heat and matter (thermos or universe) retained

**Question:**

001 10.0 points
An isolated system allows for the flow of...?

1. none of these correct
2. sound waves
3. kinetic energy
4. matter
5. heat

**Explanation:**
In the natural sciences an isolated system is a physical system without any external exchange - neither matter nor energy (as heat or work) can enter or exit, but can only move around inside.
State functions care about (how it ends - how it starts)

They don't care about path: \( \Delta \{G, H, T, V, P, n, S, U\} \)

\[
\text{If you remember the definition and don't freak out, the answer is correct.}
\]

002 10.0 points

Which of the following is true of a general thermodynamic state function?

1. The change in the value of a state function is always negative for a spontaneous reaction.

2. The value of the state function remains constant.

3. The value of a state function does NOT change with a change in temperature of a process.

4. The change of the value of a state function is independent of the path of a process. **Correct**

5. The change in the value of the state function is always positive for endothermic processes.

**Explanation:**

A change in a state function describes a difference between the two states. It is independent of the process or pathway by which the change occurs.
Thermodynamic conventions - signs/descriptions for $q$ and $w$

"Be the system"

\[ w = \int_{\text{sys}} q \ dx \]

\[ \Delta V \text{ in vacuo} \]

\[ \Delta V \text{ decrease} \]

\[ \Delta V \text{ increase} \]

\[ q \text{ endo} \]

\[ q \text{ exo} \]

You will be given a chemical and asked about a physical process involving $q + w$.

Example: $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(g)$

$\Delta G = 0$ because the reaction occurs at constant pressure. Which response is true?

1. No work is done as the reaction occurs.

2. Work is done by the system as the reaction occurs.

3. Work is done on the system as the reaction occurs. **Correct**

4. Work may be done on or by the system as the reaction occurs, depending upon the temperature.

**Explanation:**

$n_i = 9.5$ mol gas

$n_f = 6$ mol gas

For $P = \text{const}$,

$w = -P \Delta V = -(\Delta n) RT,$

$\Delta n = n_f - n_i = -3.5$ mol gas.

For $-\Delta n$, $w$ will be positive, which indicates that work was done on the system, which progresses as the reaction progresses.
heat capacity, specific heat capacity theory/application

By definition \( \Delta H = C \Delta T \) so \( C = \frac{\Delta H}{\Delta T} \)

- heat capacity is measure of ability to absorb heat into internal motion
- \( C \) is big in \( H_2O \) with vibrations, \( H \)-bands \( C = 4 J/\text{g}^\circ \text{C} \)
- specific heat is \( \Delta H = m \Delta T \) \( C = \frac{\Delta H}{m \Delta T} \) where mass (amount) matters
- \( H_2O \) has large \( C \), metals are 10 times less

004 10.0 points
Consider the following specific heats: copper, 0.384 J/g.°C; lead, 0.159 J/g.°C; water, 4.18 J/g.°C; glass, 0.502 J/g.°C. If the same amount of heat is added to identical masses of each of these substances, which substance attains the highest temperature? (Assume that they all have the same initial temperature.)

1. copper
2. water
3. lead correct
4. glass

What is difference between a, b, c heat capacities?
internal energy, enthalpy definitions & 1st law theory

you will be given several T/F statements about \(\Delta U\) and \(\Delta H\)

- 1st Law \(\Delta U_{\text{univ}} = \Delta U_{\text{sys}} + \Delta U_{\text{sur}} = 0\) energy of universe conserved
- \(\Delta U_{\text{sys}} = -\Delta U_{\text{sur}}\) from first law to basis of calculation
- \(\Delta H = \Delta U + P\Delta V\) to permit measure of \(q\) in open systems
- \(\Delta H = q_p\), \(\Delta U = q_v\)

\[\text{atm} \quad \text{closed volume}\]

005 10.0 points

Which of the following statements is/are true concerning the first law of thermodynamics?

I) The internal energy \((U)\) of the universe is conserved.
II) The internal energy of a system plus that of its surroundings is conserved.
III) The change in internal energy \((\Delta U)\) of a system and its surroundings can have the same sign.

1. I, II correct

2. III only

3. II, III

4. I only

5. I, III

6. II only

7. I, II, III

Explanation:

Statement I and II are true; the first law states that the internal energy of the universe is conserved and since the system plus the surroundings is the universe, their sum is also conserved. Statement III is false; for example, if both the system and its surroundings had a positive change in internal energy, then the internal energy of the universe would have increased or decreased - in violation of the first law.
work calculation (gases)

\[ W = -P_{ext} \Delta V \]

This is a plug and chug. Only difficulty is units. Work is typically kJ but \( P \Delta V \) is in atm so need to use conversion \( 1 \text{ atm} = 101.3 \text{ kJ} \)

**Signs:**
- If \( V \) decreases, work on system is \( + \)
- If \( V \) increases, work on surroundings is \( - \)

---

**Problem:**

006 10.0 points
1.95 mol of an ideal gas at 300 K and 3.00 atm expands from 16 L to 28 L and a final pressure of 1.20 atm in two steps:
(1) the gas is cooled at constant volume until its pressure has fallen to 1.20 atm, and
(2) it is heated and allowed to expand against a constant pressure of 1.20 atm until its volume reaches 28 L.

Which of the following is CORRECT?

1. \( w = 0 \) for the overall process
2. \( w = -6.03 \text{ kJ} \) for the overall process
3. \( w = -4.57 \text{ kJ} \) for (1) and \( w = -1.46 \text{ kJ} \) for (2)
4. \( w = 0 \) for (1) and \( w = -1.46 \text{ kJ} \) for (2) correct
5. \( w = -4.57 \text{ kJ} \) for the overall process

**Explanation:**

For step (1): If there is no change in volume, \( w = 0 \).

For step (2): For expansion against a constant external pressure,

\[
W = -P_{ext} \Delta V = (-1.2 \text{ atm})(18 \text{ L} - 6 \text{ L})
\times (101.325 \text{ J} \cdot \text{L}^{-1} \cdot \text{atm}^{-1})
= -1.45908 \text{ kJ}
\]

The total work done by the system would be the sum of the work for each step.
\[ \Delta U = q + w \] easy

Simple plug and chug. Given 2 of 3 \((\Delta U, q, w)\) solve for unknown

A CD player and its battery together do 500 kJ of work, and the battery also releases 250 kJ of energy as heat and the CD player releases 50 kJ as heat due to friction from spinning. What is the change in internal energy of the system, with the system regarded as the battery and CD player together?

1. \(-800 \text{ kJ correct}\)
2. \(+200 \text{ kJ}\)
3. \(-200 \text{ kJ}\)
4. \(-700 \text{ kJ}\)
5. \(-750 \text{ kJ}\)

Explanation:
Heat from the CD player is \(-50 \text{ kJ}\).
Heat from the battery is \(-500 \text{ kJ}\).
Work from both together on the surroundings is \(-250 \text{ kJ}\).

This question is testing your ability to see what the system is, and then look at ONLY the energy flow for the system. Here the system is the battery and the CD player together.

\[ \Delta U = q + w \]
\[ = [-50 \text{ kJ} + (-250 \text{ kJ})] + (-500 \text{ kJ}) \]
\[ = -800 \text{ kJ} \]
heat flow across phase changes calculation

Given starting and ending T, have to do between 1 and 5 calculations, then add q values up.

Example

Example

50°  →  150°  3 calculations, add 3 values up.
0°  →  50°  2 calculations

\[ q = \text{mass} \times (\Delta H_{\text{vap}}) \text{ for phase change} \]

008 10.0 points

The specific heat of liquid water is 4.184 J/g°C, and of steam 2.03 J/g°C. The heat of vaporization of water (\( \ell \)) is 2.26 kJ/g and its boiling point is 100°C. What is the total heat flow when 18 gms of water at 12°C are heated to become steam at 109°C?

1. 44.4 kJ
2. 47.6 kJ correct
3. under 28 kJ
4. 48.9 kJ
5. over 55 kJ
6. 31.7 kJ
7. 40.7 kJ
Interpreting potential energy (Rxn coordinate) diagrams

- An energy profile that is $E$ to surroundings.

Note: We don't care about the very path till kinetics in the spring.

Refer to the potential energy diagram shown below.

What is the change in enthalpy ($\Delta H$) for the reaction $A \rightarrow B$?

1. +50 kJ, endothermic **correct**
2. -50 kJ, exothermic
3. +50 kJ, exothermic
4. -250 kJ, endothermic
5. -150 kJ, endothermic

**Explanation:**

$\Delta H_1 = \Delta H_A = 250 \text{ kJ}$

$\Delta H_f = \Delta H_B = 300 \text{ kJ}$

$\Delta H = \Delta H_f - \Delta H_i$

$= 300 \text{ kJ} - 250 \text{ kJ}$

$= 50 \text{ kJ}$

Notice that $\Delta H$ is positive and therefore the reaction is endothermic.
calorimetry theory

Be able to explain how a calorimeter works and the definition of each variable in a calculation.

\[
\Delta U_{\text{sys}} = \Delta U_{\text{reactants}} = mC\Delta T_{\text{reactants}} = -\Delta U_{\text{sur}} = - (mC\Delta T_{\text{water}} + C\Delta T_{\text{calorimeter}})
\]

- More water, smaller \( \Delta T \)
- Large \( C_{\text{H}_2\text{O}} \), smaller \( \Delta T \)
- \( C_{\text{calorimeter}} \) is heat capacity in J/°C, \( C_{\text{H}_2\text{O}} \) is specific heat in J/°C

Which of the following is NOT a feature of the bomb calorimetry apparatus used to measure the internal energy of a reaction?

1. The heat capacity of the calorimeter should be known to accurately correct for any heat lost to it.

2. The thermometer is inserted directly into the reaction vessel to measure \( \Delta T \) of the reaction. **Correct**

3. Large quantities of water surrounding the reaction vessel absorb the majority of the heat loss.

4. The volume of the reaction vessel is held constant to eliminate energy released as work.

5. The large heat capacity of water is beneficial in measuring heat released by combustion reactions.

**Explanation:**

The thermometer is placed in the water that surrounds the reaction vessel.
calorimetry calculation

\[
\Delta U_{sys} = \Delta U_{sum} = -\left( m \text{ CAT} + \text{ CAT}_\text{colorite} \right)
\]

- easy plug and chug using \( \Delta T \) twice
- two \( \text{C}_\text{H}_2\text{O} \), calculate values
- convert \( l \) to \text{ml} to grams
- usual answer is per amount like J/cheetos or kJ/gram

011 10.0 points
A 1.00 g sample of n-hexane (C\textsubscript{6}H\textsubscript{14}) undergoes complete combustion with excess O\textsubscript{2} in a bomb calorimeter. The temperature of the 1502 g of water surrounding the bomb rises from 22.64°C to 29.30°C. The heat capacity of the hardware component of the calorimeter (everything that is not water) is 4042 J/°C. What is \( \Delta U \) for the combustion of \text{n-C}_6\text{H}_{14}? \text{One mole of } n\text{-C}_6\text{H}_{14} \text{ is 86.1 g. The specific heat of water is } 4.184 \text{ J/g°C}.\n
1. \(-1.15 \times 10^4 \text{ kJ/mol}\)
2. \(-4.52 \times 10^3 \text{ kJ/mol}\)
3. \(-7.40 \times 10^4 \text{ kJ/mol}\)
4. \(-5.92 \times 10^3 \text{ kJ/mol} \text{ correct}\)
5. \(-9.96 \times 10^3 \text{ kJ/mol}\)

**Explanation:**

\[
m_{\text{C}_6\text{H}_{14}} = 1.00 \text{ g} \quad m_{\text{water}} = 1502 \text{ g} \\
\text{SH} = 4.184 \text{ J/g°C} \quad \text{HC} = 4042 \text{ J/°C} \\
\Delta T = 29.30°C - 22.64°C = 6.66°C
\]

The increase in the water temperature is 29.30°C - 22.64°C = 6.66°C. The amount of heat responsible for this increase in temperature for 1502 g of water is

\[
q = (6.66°C) \left( \frac{4.184 \text{ J}}{\text{g°C}} \right) (1502 \text{ g}) \\
= 41854 \text{ J} = 41.85 \text{ kJ}
\]

The amount of heat responsible for the warming of the calorimeter is

\[
q = (6.66°C)(4042 \text{ J/°C}) \\
= 26920 \text{ J} = 26.92 \text{ kJ}
\]

The amount of heat released on the reaction is thus 41.85 kJ + 26.92 kJ = 68.77 kJ per g of n-hexane.

Per mol of n-hexane, this becomes

\[
\left( 68.77 \frac{\text{kJ}}{\text{g}} \right) \left( \frac{86.1 \text{ g}}{\text{mol}} \right) = 5921 \text{ kJ/mol}
\]
formation constants definition easy

"Elements in their Standard States"

room temp and pressure

H₂, C, O, N

are combined to form a compound (1 mole)

Example:

\[ \frac{3}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \]

\[ \frac{3}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \]

\[ \text{H}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \]

\[ \text{H}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \]

Which of the reactions below is a formation reaction?

1. \[ \text{H}_2(\text{g}) + \text{C}_{\text{graphite}}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \]

2. \[ 2\text{H}_2(\text{g}) + 2\text{C}_{\text{graphite}}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CH}_3\text{O}(\text{ℓ}) \]

3. \[ 2\text{Fe}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) \text{ correct} \]

4. \[ \text{N}_2(\text{ℓ}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2\text{H}_4(\text{ℓ}) \]

Explanation:

A formation reaction produces exactly one mole of one product from elements in their standard states.
Hess' law - Rxn enthalpies

This is hard because it is messy. Rewrite the problem to clean it up with reaction and cancel them out to add up \( \Delta H_{\text{rxn}} \).

\[ \begin{align*}
1. \quad & \ 2A + B \rightarrow C \quad \Delta H_{\text{rxn}} = 20 \\
2. \quad & \ D \rightarrow C \quad \Delta H_{\text{rxn}} = 50 \\
3. \quad & \ 2A + B \rightarrow 2D \\
\end{align*} \]

Then multiply through with +/- and coefficients to cancel all but find compound.

Calculate the standard reaction enthalpy for the reaction:

\[ \text{N}_2\text{H}_4(\ell) + \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g}) \]

\[ \begin{align*}
\text{given} & \\
\text{N}_2\text{H}_4(\ell) + \text{O}_2(\text{g}) & \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \\
\Delta H^\circ = -543 \text{ kJ} \cdot \text{mol}^{-1} \\
2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) & \rightarrow 2\text{H}_2\text{O}(\text{g}) \\
\Delta H^\circ = -484 \text{ kJ} \cdot \text{mol}^{-1} \\
\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) & \rightarrow 2\text{NH}_3(\text{g}) \\
\Delta H^\circ = -92.2 \text{ kJ} \cdot \text{mol}^{-1} \\
\end{align*} \]

1. -1119 kJ \cdot \text{mol}^{-1} \\
2. -151 kJ \cdot \text{mol}^{-1} \text{ correct} \\
3. -935 kJ \cdot \text{mol}^{-1} \\
4. -243 kJ \cdot \text{mol}^{-1} \\
5. -59 kJ \cdot \text{mol}^{-1} \\

Explanation:

We need to reverse the second reaction and add them:

\[ \begin{align*}
\text{N}_2\text{H}_4(\ell) + \text{O}_2(\text{g}) & \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \\
\Delta H = -543 \text{ kJ/mol} \\
2\text{H}_2\text{O}(\text{g}) & \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \\
\Delta H = +484 \text{ kJ/mol} \\
\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) & \rightarrow 2\text{NH}_3(\text{g}) \\
\Delta H = -92.2 \text{ kJ/mol} \\
\end{align*} \]

\[ \begin{align*}
\text{N}_2\text{H}_4(\ell) + 3\text{H}_2(\text{g}) & \rightarrow 2\text{H}_2(\text{g}) + 2\text{NH}_3(\text{g}) \\
\Delta H = -151.2 \text{ kJ/mol} \\
\text{N}_2\text{H}_4(\ell) + \text{H}_2(\text{g}) & \rightarrow 2\text{NH}_3(\text{g}) \\
\Delta H = -151 \text{ kJ/mol} \\
\end{align*} \]
Hess' law - bond energy  

- Easy but messy  
- $2H_2 + O_2 \rightarrow 2H_2O$

- Give table of BE on front page
- Write the Lewis structures bond by bond
- Label each bond with B.E.
- Add up reactants $436 \times 2 + 498$ and products $4 \times 463$
- $\sum$ Reactants $- \sum$ Products $= \Delta E \approx -500$ (actual is -482)
- Don't overround off, take your time with math

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014 10.0 points

Estimate the heat released when ethene ($\text{CH}_2\equiv\text{CH}_2$) reacts with HBr to give CH$_3$CH$_2$Br.

1. 200 kJ/mol
2. 76 kJ/mol correct
3. 1036 kJ/mol
4. 424 kJ/mol
5. 470 kJ/mol

Explaination:

$$\Delta H = \sum E_{\text{break}} - \sum E_{\text{make}}$$

$$= [(\text{C}\equiv\text{C}) + (\text{H} \equiv \text{Br})]$$
$$- [(\text{C} \equiv \text{H}) + (\text{C} \equiv \text{Br}) + (\text{C} \equiv \text{C})]$$
$$= (602 \text{ kJ/mol} + 366 \text{ kJ/mol})$$
$$- [413 \text{ kJ/mol} + 285 \text{ kJ/mol}$$
$$+ 346 \text{ kJ/mol}]$$
$$= -76 \text{ kJ/mol},$$

so 76 kJ/mol of heat was released.
For a given set of conditions be able to assign

\[ \Delta S_{\text{min}} \quad \Delta G_{\text{sys}} \quad \Delta H_{\text{sys}} \quad \Delta S_{\text{sys}} \quad \Delta S_{\text{surr}} \quad q \quad W \]

happens   happens   endo   gas is   opposite   make gas
happens   messy   sign of \( \Delta H_{\text{sys}} \)   heat into
happens   \( \Delta S_{\text{surr}} \)   work or

For example if given a phase change producing gas at high T then the signs are as shown starting with
\[ \Delta H_{\text{sys}} \oplus, \Delta S_{\text{sys}} \oplus \] because that is clue given.
And we because gas formed in clue

015 10.0 points
Consider a reaction that is non-spontaneous at all temperatures. What would be the signs of \( \Delta G_{\text{sys}} \), \( \Delta H_{\text{surr}} \), and \( \Delta S_{\text{min}} \) respectively for such a reaction?

1. +, +, +
2. -, +, -
3. +, -, - correct
4. -, +, +
5. +, +, +

Explanation:
For a reaction that is non-spontaneous at all temperatures, the free energy of the system will increase and the entropy of the universe will decrease. Such a reaction must be endothermic, and the heat it gains will be lost from the surroundings.
Given a collection of compounds, rank $S^\circ$ using logic:

- $S \rightarrow l \rightarrow g$ is large $S^\circ$
- small $\rightarrow$ large $\rightarrow$ large $S^\circ$
- simple $\rightarrow$ complicated $\rightarrow$ large $S^\circ$

Examples:
- $H_2O(s) < H_2O(l) < H_2O(g)$

Which one shows the substances in the decreasing order of their molar entropy?

1. C(s), H$_2$O(l), H$_2$O(g), H$_2$O(s)
2. H$_2$O(g), H$_2$O(l), H$_2$O(s), C(s) **correct**
3. None of these
4. H$_2$O(s), H$_2$O(l), H$_2$O(g), C(s)
5. C(s), H$_2$O(g), H$_2$O(l), H$_2$O(s)
6. C(s), H$_2$O(s), H$_2$O(l), H$_2$O(g)

**Explanation:**
Gases will have a higher entropy than liquids so we expect H$_2$O(l) to have the lowest molar entropy. The gases will increase in entropy in the order Ne(g) < Ar(g) < CO$_2$(g). Ne and Ar are both atoms so they should have less entropy than a molecular substance, which has more complexity. Ar will have a higher entropy than Ne because it has a larger mass and more fundamental particles. The correct order is

H$_2$O(l) < Ne(g) < Ar(g) < CO$_2$(g).
predicting changes in entropy

Given a series of chemical and physical processes, predict sign of \( \Delta S_{sys} \):

\[
\begin{align*}
S & \rightarrow l \rightarrow g \quad \Delta S > 0 \\
g & \rightarrow l \rightarrow S \quad \Delta S < 0
\end{align*}
\]

017 10.0 points

Consider the following processes. (Treat all gases as ideal.)

I) The pressure of one mole of oxygen gas is allowed to double isothermally.

II) Carbon dioxide is allowed to expand isothermally to 10 times its original volume.

III) The temperature of one mole of helium is increased 25°C at constant pressure.

IV) Nitrogen gas is compressed isothermally to one half its original volume.

V) A glass of water loses 100 J of energy reversibly at 30°C.

Which of these processes leads to an increase in entropy?

1. III and V
2. I and II
3. I and IV
4. V
5. II and III correct
What is the entropy at \( T = 0 \) K for one mole of chloroform (CHCl₃)?

1. \( 1.9 \times 10^{-23} \) J K⁻¹
2. \( 1.38 \) J K⁻¹
3. \( 11.5 \) J K⁻¹ correct
4. \( -11.5 \) J K⁻¹
5. \( 0 \) J K⁻¹

Explanation:
Since the question is concerned with the residual entropy of a mole of chloroform, which as 4 orientations, we can use the Boltzmann equation to calculate the residual entropy.

\[
S = N_a k \ln W = R \ln 4 = 11.5 \text{ J K}^{-1}
\]
\[
\text{stat thermo internal energy medium}
\]

Remember:
- Each atom = 3 modes × \( \frac{1}{2} kT \) = \( \frac{3}{2} kT \) kinetic energy
- Each molecule = \( \frac{3}{2} kT \times \# \text{atoms} \) internal energy
- Every molecule has \( \frac{3}{2} kT \) translation + \( \frac{3}{2} kT \) rotation (unless linear)
- Left over energy is vibration

Example: 5 moles \( \text{CH}_3\text{Cl} \) has \( \frac{3}{2} kT \) translate + \( \frac{3}{2} kT \) rotate per mole-

\[
\frac{15}{2} kN T = \frac{15}{2} R T + \frac{15}{2} k N T = \frac{15}{2} R T
\]

\( \text{or for translate and rotation together} \)

---

**019 10.0 points**

What is the total non-vibrational internal energy of 10 nitrous oxide (\( \text{N}_2\text{O} \)) molecules?

1. 15 kT
2. 10 kT
3. 25 kT correct
4. 10 RT
5. 25 RT

**Explanation:**

- 10 molecules times \( \frac{3}{2} kT \) total translational energy per molecule is \( \frac{30}{2} kT \) is 15 kT.
- Since nitrous oxide is a linear molecule, its rotational energy is 10 molecules times kT is 10 kT. The total non-vibrational energy is 25 kT.
second law theory

Here are some truths:

- \( \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} \) \( \geq 0 \) happens.

- \( \Delta S = \frac{Q}{T} \) which means \( \Delta S \) is larger for high \( Q \) and low \( T \).

- So exploding a 
    
    - H2 balloon at North pole is big \( \Delta S \).

- \( \Delta G = -T \Delta S_{\text{univ}} \) is how we get to use \( \Delta S_{\text{sys}} \) rather than \( \Delta S_{\text{univ}} \).

- \( \Delta S_{\text{univ}} = -\frac{\Delta H_{\text{sys}}}{T} \) is how heat from exothermic reaction makes chaos in surroundings.

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020 10.0 points

Advertising claims sometimes state that adding something mechanical to a car's engine will allow it to recover 100% of the energy that comes from burning gasoline. You should be skeptical of such claims because they violate the

1. first law of thermodynamics.

2. activation energy requirements of all chemical reactions.

3. law of conservation of matter.

4. second law of thermodynamics. **correct**

**Explanation:**

If you burn gasoline in an engine to move a car, you are ultimately converting chemical potential energy into kinetic energy. But much of this energy is lost as heat. There is NO way to make any energy conversion 100% efficient.
second law calculation (ΔS of surroundings) medium

In calculating \( \Delta S_{\text{sur}} \), \( \Delta S_{\text{sys}} \) comes from table of molar entropies.

But \( \Delta S_{\text{sur}} \) comes from table of \( \Delta H_{\text{rxn}} \)

\[
\Delta S_{\text{sur}} = -\frac{\Delta H_{\text{sys}}}{T}
\]

- Make sure signs are right, \( \Delta S_{\text{sur}} \) opposes \( \Delta H_{\text{sys}} \)
- Get units right. Use J for energy, not K

Example: What is \( \Delta S_{\text{sur}} \)?

\[
\Delta S_{\text{sys}} = \pm 22 \text{ J/K}
\]

\[
\Delta S_{\text{sur}} = -\frac{-6000 \text{ J}}{298 \text{ K}} = +30 \text{ J/K}
\]

\( \Delta H_{\text{rxn}}^\circ = 6 \text{ kJ at 298K} \quad \text{and} \quad \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(s) \)

- Note you don’t use \( \Delta S_{\text{sys}} \)
- Note \( l \rightarrow s \) is exo so use \(-6000\) not \(+6000\)
- Note \( \Delta S_{\text{sur}} \) became exothermic

---

021 10.0 points
Calculate \( \Delta S_{\text{sur}}^\circ \) at 298 K for the reaction

\[ 6 \text{ C(s) + 3 H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\ell) \]

\( \Delta H_{\text{r}}^\circ = +49.0 \text{ kJ} \cdot \text{mol}^{-1} \) and \( \Delta S_{\text{r}}^\circ = -253 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \).

1. \(- 417 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\)
2. \(- 164 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\) correct
3. \(+ 253 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\)

Explanation:

\[
\Delta H_{\text{r}}^\circ = 49000 \text{ J} \cdot \text{mol}^{-1} \quad T = 298 \text{ K}
\]

\[
\Delta S_{\text{sur}}^\circ = \frac{q_{\text{sur}}}{T} = -\frac{q}{T} = -\frac{-\Delta H_{\text{r}}^\circ}{298 \text{ K}} = -\frac{-49000 \text{ J} \cdot \text{mol}^{-1}}{298 \text{ K}} = -164.43 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\]
relating reaction spontaneity to \( T \) for phase changes

\[
\Delta G = \Delta H - T\Delta S = 0 \quad \text{at phase change so}
\]

\[
\Delta H = T\Delta S
\]

\[
T_{\text{phase}} = \frac{\Delta H}{\Delta S}
\]

- be careful with units of \( T \)
- \( K \) vs \( ^\circ C \)
- note how similar question 21 is.

Explaination:

The process is spontaneous, which means \( \Delta S_{\text{universe}} > 0 \) according to the Second Law of Thermodynamics.

Entropy (\( S \)) is high for systems with high degrees of freedom, disorder or randomness and low for systems with low degrees of freedom, disorder or randomness.

\[
S(g) > S(\ell) > S(s)
\]

The system is

\[
\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(g)
\]

so \( \Delta S_{\text{system}} > 0 \).

The entropy of the surroundings must be negative. Energy is removed from the surroundings to get the water to evaporate.
relating reaction spontaneity to $T$ for chemical reactions

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

+ + always happens
+ - never happens
- + always happens
- - happens low $T$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sw}}$$

+ + always
+ - happens high $T$
+ - happens low $T$
- - never

For a process, be able to assess
$\Delta S_{\text{univ}}, \Delta S_{\text{sys}}, \Delta S_{\text{sw}}, \Delta G_{\text{sys}}, \Delta H_{\text{sys}}$

Examples

$$\text{C}_6\text{H}_6\text{g} + 2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O}_l$$

$\Delta H_{\text{sys}} \Theta$ combustion, $\Delta S_{\text{sys}} \Theta$ $q \rightarrow l$

so $\Delta S_{\text{sw}} \Theta$, $\Delta S_{\text{univ}}$, and $\Delta G_{\text{sys}}$ at low $T$

Example

$$\text{H}_2\text{O}_g \rightarrow \text{H}_2\text{O}_l$$

$\Delta G \Theta$, $\Delta S_{\text{univ}} \Theta$, $\Delta S_{\text{sys}} \Theta$, $\Delta H_{\text{sys}} \Theta$, $\Delta S_{\text{sw}} \Theta$

Note: happens low $T$ (<100°C)

For the reaction

$$2\text{SO}_3\text{(g)} \rightarrow 2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)}$$

$\Delta H^o = +198$ kJ mol$^{-1}$ at 298 K. Which statement is true for this reaction?

1. The reaction is driven by the enthalpy.

2. The reaction will not be spontaneous at any temperature.

3. The reaction will not be spontaneous at high temperatures.

4. $\Delta G^o$ will be positive at high temperatures.

5. $\Delta G^o$ will be negative at high temperatures. correct

Explanation:

$\Delta G = \Delta H - T \Delta S$ is used to predict spontaneity. ($\Delta G$ is negative for a spontaneous reaction.) $\Delta H$ is positive and $T$ is always positive. For the reaction 2 mol gas $\rightarrow$ 3 mol gas. The more moles of gas, the higher the disorder, so $\Delta S$ is positive and $\Delta G = (+) - T(+)$.

For $\Delta G$ to be negative, $T$ must be large.


\[ \Delta G_{\text{rxn}} \text{ from table values calculation} \]

Given a chemical reaction:

\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \]

\[ \Delta H = \Sigma \Delta H_{\text{prod}} - \Sigma \Delta H_{\text{react}} \]

\[ \Delta S = \Sigma S_{\text{prod}} - \Sigma S_{\text{react}} \]

\[ \Delta S = \frac{2 \times 70}{2} - \left[ \frac{2 \times 130}{2} + 2 \times 205 \right] \]

\[ = 140 - 146 = -6 \]

\[ \Delta G_{\text{rxn}} = \Delta H - T \Delta S \]

\[ = -572 \text{kJ} \]

\[ \text{Hint}: \text{Combustion reaches } \Delta G \to -572 \text{kJ} \]

\[ \text{Hint}: T \Delta S \text{ is usually small so } \Delta H \approx \Delta G \]

\[ \text{Just sayin...} \]

024 10.0 points

What is \( \Delta G^\circ \) for the combustion of liquid n-pentane?

1. 3389 kJ/mol
2. -383 kJ/mol
3. 383 kJ/mol
4. -3389 kJ/mol correct
5. -451 kJ/mol
6. 451 kJ/mol

\[ \text{C}_5\text{H}_{12}(l) + 8 \text{O}_2(g) \rightarrow 5 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) \]

\[ \Delta H = \left[ 5 \times (-394) + 6 \times (-286) \right] \text{kJ/mol} \]

\[ - \left[ 1 \times (-174) + 8 \times (0) \right] \text{kJ/mol} \]

\[ = -3512 \text{kJ/mol} \]

and

\[ \Delta S = \left[ 5 \times 214 + 6 \times 70 \right] \text{J/mol} \cdot \text{K} \]

\[ - \left[ 1 \times 263 + 8 \times 205 \right] \text{J/mol} \cdot \text{K} \]

\[ = -413 \text{J/mol} \cdot \text{K} \]

\[ = -0.413 \text{kJ/mol} \cdot \text{K} \]

\[ \Delta G = \Delta H - T \Delta S \]

\[ = -3512 \text{kJ/mol} \]

\[ - (298 \text{K}) \times (-0.413 \text{kJ/mol} \cdot \text{K}) \]

\[ = -3389 \text{kJ/mol} \]
predicting compound stability from $\Delta G_f$

If $\Delta G_f^0 < 0$ then compound is stable.
If $\Delta G_f^0 > 0$ then compound not stable.

---

025 10.0 points

Consider the data below regarding different allotropes of carbon.

<table>
<thead>
<tr>
<th>Carbon Allotrope</th>
<th>$\Delta G_f^0$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(s, graphite)</td>
<td>0</td>
</tr>
<tr>
<td>C(s, diamond)</td>
<td>2.9</td>
</tr>
<tr>
<td>C$_{60}$(s, buckminsterfullerene)</td>
<td>24</td>
</tr>
</tbody>
</table>

Which of the following statements is supported by these data?

1. C$_{60}$ is thermodynamically more stable than graphite under standard conditions.

2. Graphite could spontaneously form C$_{60}$ under standard conditions.

3. Formation of graphite from C$_{60}$ would be exergonic under standard conditions. correct

4. Diamond is the least thermodynamically stable allotrope of carbon under standard conditions.

---

Example:
Diamond as $\Delta G_f^0 = +3$ kJ/mole
so not stable.
Benzene $\Delta G_f^0 = +4.9$ kJ
so not stable.
Ethylene $\Delta G_f^0 = -2.78$ kJ
so stable.