

0. Graphite is thermodynamically less stable than diamond under standard conditions.
1. True
 2. False

Graphite is thermodynamically more stable than diamond under standard conditions.

1. Which statement would be the best interpretation of the First Law of Thermodynamics?
1. The total amount of energy in the universe is increasing.
 2. The total amount of entropy in the universe is increasing.
 3. The total amount of energy in the universe is constant.
 4. The total amount of matter in the universe is constant.

The first law is the law of conservation of energy and mass (not matter). The second law deals with entropy.

2. Enthalpy (H) is best defined by which of the following statements?
1. the capacity of a system to influence the entropy of its surroundings
 2. pressure-volume work
 3. a measure of a system's energetic degeneracy
 4. none of these describe enthalpy

We know that the change in enthalpy of a system (whether it increases or decreases in a given system for a given process) affects the entropy of its surroundings, thereby influencing the spontaneity of a reaction.

- 3.1. Water changing from a solid to a liquid is
1. an endothermic change.
 2. an exothermic change.
 3. Neither an exothermic or an endothermic change

Heat is always required for melting any substance. Melting is an endothermic process.

- 3.2. Heat flow is considered positive when heat flows (into, out of) a system; work is considered positive when work is done (by, on) a system.
1. out of; by
 2. into; on
 3. out of; on
 4. into; by

Heat flow q is considered positive when heat flows into a system. Work w is considered positive when work is done on a system.

4. Definition: state functions

An extensive state function's value is (dependent on/independent of) the amount of a given substance. An intensive state function's value is (dependent on/independent of) the amount of a given substance.

1. dependent on, dependent on
2. independent of, independent of
3. dependent on, independent of
4. independent of, dependent on

Extensive properties depend on the extent of the system (whence the term extensive); intensive properties do not.

5. What is the enthalpy change for $\Delta H^\circ_f(\text{C}(s, \text{graphite}))$?
1. -1300 kJ/mol
 2. 31 kJ/mol
 3. 717 kJ/mol
 4. 0 kJ/mol
 5. -575 kJ/mol

For an element in its standard state at 25 °C, 1 atm, $\Delta H^{\circ}_f = \text{zero}$.

6. 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. lead
2. water
3. glass
4. copper

Lead has the lowest specific heat, and thus requires the least heat in order to have an increase in temperature. Its temperature will thus increase the most for a given amount of heat.

7.1. You set up a bomb calorimetry experiment using 1 liter of water as your heat sink and combusting a 4.409 g sample of propane (C₃H₈). If the initial and final temperature are 24.90 °C and 77.96 °C respectively, what is the approximate molar enthalpy of combustion of ethene? (Assume the calorimeter itself absorbs no heat. Assume the density of water is 1 g·mL⁻¹)

1. -222.0 kJ · mol⁻¹
2. -222, 000 kJ · mol⁻¹
3. -22.20 kJ · mol⁻¹
4. -22, 200 kJ · mol⁻¹
5. -2, 220 kJ · mol⁻¹

$$\Delta T = T_f - T_i = 77.96 \text{ }^{\circ}\text{C} - 24.90 \text{ }^{\circ}\text{C} = 53.06 \text{ }^{\circ}\text{C} = 53.06 \text{ K}$$

$$m = 1 \text{ L} \cdot (1000 \text{ mL/L}) \cdot (1.00 \text{ g/mL}) = 1000 \text{ g}$$

$$n = 4.409 \text{ g propane} \cdot (1 \text{ mol}/44.09 \text{ g}) = 0.1 \text{ mol propane}$$

$$-\Delta H_{\text{rxn}} = \Delta H_{\text{cal}} = mc\Delta T = 1000 \text{ g} \cdot 4.184 \cdot 53.06 \text{ K} = 220 \text{ kJ}$$

$$-220 \text{ kJ} / 0.1 \text{ mol} = -2, 220 \text{ kJ} \cdot \text{mol}^{-1}$$

7.2. A 0.10 g piece of chocolate cake is combusted with oxygen in a bomb calorimeter. The temperature of 4,000 g of H₂O in the calorimeter is raised by 0.32 K. (The specific heat of the water is 1.0 cal/g·K and the heat of vaporization of water is 540 cal/g.) What is ΔE for the combustion of chocolate cake? Assume no heat is absorbed by the calorimeter.

1. -460 kcal/g
2. -532 kcal/g
3. -13.3 kcal/g
4. -12.8 kcal/g
5. -3900 kcal/g

$$m_{\text{water}} = 4000 \text{ g}$$

$$m_{\text{cake}} = 0.10 \text{ g}$$

$$\Delta T = 0.32 \text{ K}$$

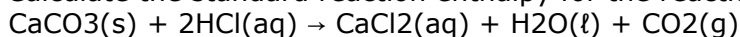
$$\Delta H_{\text{vap}} = 540 \text{ cal/g}$$

$$c = 1.0 \text{ cal/g}\cdot\text{K}$$

The amount of heat responsible for the increase in water temperature for 4000 g of water is $q = 1.0 \cdot (4000)(0.32) = 1280 \text{ cal}$

The amount of heat released by the reaction is thus 1280 cal. There were 0.10 g of cake, so $-1280 \text{ cal} / 0.10 \text{ g} \text{ (kcal} / 1000 \text{ cal)} = -12.8 \text{ kcal/g}$

8. Calculate the standard reaction enthalpy for the reaction of calcite with hydrochloric acid:



The standard enthalpies of formation are:

for CaCl₂(aq) : -877.1 kJ/mol;

for $\text{H}_2\text{O}(\ell)$: -285.83 kJ/mol ;
for $\text{CO}_2(\text{g})$: -393.51 kJ/mol ;
for $\text{CaCO}_3(\text{s})$: -1206.9 kJ/mol ;
and for $\text{HCl}(\text{aq})$: -167.16 kJ/mol .

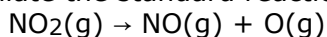
1. -72.7 kJ/mol
2. -165 kJ/mol
3. -38.2 kJ/mol
4. -98.8 kJ/mol
5. -15.2 kJ/mol
6. -116 kJ/mol
7. -215 kJ/mol

We use Hess' Law:

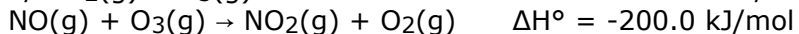
$$\Delta H^\circ = \sum H^\circ_{\text{f,prod}} - \sum H^\circ_{\text{f,react}} = -15.22 \text{ kJ/mol} .$$

9. Calculation: Hess's Law and combined reaction enthalpies

Calculate the standard reaction enthalpy for the reaction:



Using:



1. $+592 \text{ kJ/mol}$
2. $+555 \text{ kJ/mol}$
3. $+307 \text{ kJ/mol}$
4. $+355 \text{ kJ/mol}$
5. $+192 \text{ kJ/mol}$

$$\Delta H_{\text{rxn}} = \frac{1}{2}(498.4) + -1(142.7) + -1(200.0) = +306.5$$

10.1. How much internal energy would be associated with the rotational motion of 1 mole of CO_2 ?

1. RT
2. $\frac{1}{2} RT$
3. $\frac{3}{2} RT$
4. $2 RT$

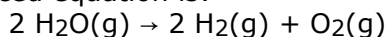
Since carbon dioxide is linear, it has two rotational modes, times $\frac{1}{2} RT$ per mode per mole gives a total of RT .

10.2. What would be the total vibrational energy of .0833 moles of cetane ($\text{C}_{16}\text{H}_{34}$), assuming cetane is non-linear?

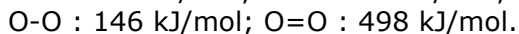
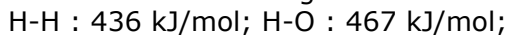
1. $72 RT$
2. $144 RT$
3. $12 RT$
4. $6 RT$

Cetane will have 150 total modes, 144 of which are vibrational, times $\frac{1}{2} RT$ per mode per mole times 0.0833 moles gives a total of $6 RT$.

11. What energy change is associated with the reaction to obtain 1.00 mole of H_2 ? The balanced equation is:



and the relevant bond energies are:



1. $+425 \text{ kJ}$

2. +249 kJ
3. -425 kJ
4. +498 kJ
5. -498 kJ
6. -436 kJ

$$\Delta H = \sum BE_{\text{react}} - \sum BE_{\text{prod}} = 1868 \text{ kJ/mol} - 1370 \text{ kJ/mol} = 498 \text{ kJ/mol}$$

The reaction forms 2 moles of H₂, so the energy to form one mole of H₂ from one mole of water vapor is half as much: 249 kJ/mol.

12.1. 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?

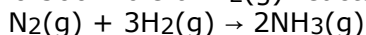
1. $w = -4.57 \text{ kJ}$ for the overall process
2. $w = -6.03 \text{ kJ}$ for the overall process
3. $w = -4.57 \text{ kJ}$ for (1) and $w = -1.46 \text{ kJ}$ for (2)
4. $w = 0$ for the overall process
5. $w = 0$ for (1) and $w = -1.46 \text{ kJ}$ for (2)

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

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

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

12.2. 0.500 mole of N₂(g) reacts with 1.50 moles H₂(g) to produce NH₃(g):



If this reaction is carried out in a system against a constant 0.75 atm pressure (i.e., a piston) at 0 °C, calculate the magnitude of the P V work.

1. $2.27 \times 10^3 \text{ J}$
2. 22.4 J
3. 22.7 J
4. $22.4 \times 10^3 \text{ J}$
5. $4.54 \times 10^3 \text{ J}$

$$w = -\Delta nRT = -(-1) (8.314) (273\text{K}) = 2269.72 \text{ J/mol}$$

13. Which of the following are not forms of internal energy?

1. motion of molecules
2. kinetic energy
3. heat
4. potential energy
5. chemical bonds

Heat is a process function, a means by which energy is transferred between systems and surroundings, but it is not a form of internal energy.

14. Which of the following statements concerning calorimetry is/are true?

- I) Bomb calorimeters hold the volume of the system constant.
- II) The calorimeter itself does not absorb heat.
- III) $\Delta H = q$ in a bomb calorimeter.

1. I, II
2. I only
3. II only
4. I, II, III
5. I, III

6. II, III
7. III only

Volume is constant in a bomb calorimeter; $q_v = \Delta E$ not ΔH . The apparatus does absorb heat, even though we sometimes ignore this for the sake of convenience.

15. A system did 150 kJ of work and its internal energy increased by 60 kJ. How much energy did the system gain or lose as heat?

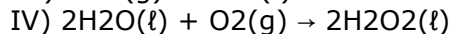
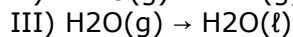
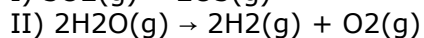
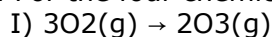
1. The system gained 60 kJ of energy as heat.
2. The system gained 90 kJ of energy as heat.
3. The system gained 210 kJ of energy as heat.
4. The system lost 90 kJ of energy as heat.
5. The system lost 210 kJ of energy as heat.

$$\Delta E = q + w$$

$$60 = q - 150$$

$$q = 210 \text{ kJ}$$

16.1. For the four chemical reactions



which one(s) is/are likely to exhibit a positive ΔS ?

1. All have a positive ΔS .
2. I, III and IV only
3. I and II only
4. III and IV only
5. II only

The Third Law of Thermodynamics states that the entropy of a perfect pure crystal at 0 K is 0. As disorder, randomness, and degrees of freedom increase, so does S . Entropy can increase by changing phase from solid to liquid to gas, and by increasing temperature, volume, or number of particles. In reaction I, the final state has less gas particles (and thus less entropy) than the initial state. Therefore ΔS is negative. In reaction II, the final state has more gas particles (and thus more entropy) than the initial state. Therefore ΔS is positive. III describes a phase change. Gases have more degrees of freedom, randomness, and disorder (entropy) than liquids. The final state is a liquid and the initial state is a gas. Therefore ΔS is negative. In reaction IV, the final state has 0 gas particles and the initial state has 1 mole of gas particles. Therefore ΔS is negative.

16.2. When Δn_{gas} for a reaction is large and positive ΔS for the reaction is likely to be (large/small) and (positive/negative).

1. large, positive
2. large, negative
3. small, positive
4. small, negative

An increase in moles of gas leads to an increase in entropy; the relative magnitudes of Δn_{gas} and ΔS are proportional.

17. Which of the following would have the largest absolute entropy?

1. $\text{N}_2(\text{g})$
2. $\text{N}_2(\text{s})$
3. $\text{N}_2(\text{aq})$ (nitrogen dissolved in water)
4. $\text{N}_2(\ell)$

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. Gases have more degrees of freedom, disorder and randomness than aqueous solutions, liquids, or solids.

18. Calculate the standard entropy of fusion of ethanol at its melting point 159 K. The standard molar enthalpy of fusion of ethanol at its melting point is $5.02 \text{ kJ} \cdot \text{mol}^{-1}$.

1. $-5.02 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
2. $-44.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
3. $-31.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
4. $+31.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
5. $+5.02 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$$\Delta H_{\text{fus}} = 5020 \text{ J} \cdot \text{mol}^{-1}$$

$$T_{\text{MP}} = 159 \text{ K}$$

$$\Delta S_{\text{cond}} = q/T = \Delta H_{\text{fus}} / T_{\text{MP}} = 5020 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} / 159 \text{ K} = +31.5723 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

19.1. Which of the following statements is FALSE?

1. The total amount of energy and matter in the Universe is constant.
2. Breaking chemical bonds is an endothermic process.
3. It is more efficient to use a primary energy source than a secondary energy source.
4. Entropy must be conserved in all chemical reactions.

The Second Law of Thermodynamics states that in spontaneous changes the universe tends toward a state of greater disorder. Entropy is not conserved.

19.2. Which of these statements about thermodynamics is NOT TRUE?

1. The entropy of the system is always increasing.
2. Energy is conserved in chemical reactions.
3. Heat given off to the surroundings is negative in sign.
4. ΔV , ΔS , and ΔH are examples of changes in thermodynamic state functions.
5. Work done on the system is positive in sign.

The entropy of a system or its surroundings may increase or decrease. The Second Law of Thermodynamics states that in spontaneous changes, the universe tends toward a state of greater disorder; that is, entropy increases ($\Delta S_{\text{univ}} > 0$).

20. The law states that a substance that is perfectly crystalline at 0 K has an entropy of zero. This law is called

1. None of these
2. the first law of thermodynamics.
3. the third law of thermodynamics.
4. the second law of thermodynamics.
5. the zeroth law of thermodynamics.

The Third Law of Thermodynamics states that the entropy of a pure crystalline substance is 0 at absolute 0 K.

21. In terms of absolute entropy, which of the following is/are true?

- I) W has both a real and a theoretical value.
 - II) The Boltzmann constant *can* be used when calculating S for molar quantities.
 - III) W for 1 mole of CO is greater than W for 1 mole of O₂.
1. III only
 2. I and III
 3. I, II and III
 4. II only
 5. I and II
 6. I only
 7. II and III

All of these statements are true.

22. Which of the following systems would likely have the greatest residual entropy at absolute zero?

1. 10 BH₂F molecules
2. 20 CCl₄ molecules
3. 9 CHCl₃ molecules
4. 100 BF₃ molecules

9 CHCl₃ molecules would have the greatest value for W (4⁹).

23. What is the positional entropy at absolute zero for two moles of CF₃Cl?

1. 11.5 J/K
2. 5.7 J/K
3. 0 J/K
4. 8.3 J/K
5. 23 J/K

CF₃Cl has 4 possible orientations, so there are $W = 4(2 \text{ mol}) \cdot N_A$ microstates.

$S = k \ln W = (2 \text{ mol}) N_A k \ln 4$

$= (2 \text{ mol}) (6.02 \times 10^{23} \text{ mol}^{-1}) \times (1.38 \times 10^{-23} \text{ J/K}) \ln 4 = 23.0336 \text{ J/K}$

24.1. What is the ΔS_{surr} when a balloon filled with 8 grams of hydrogen is combusted at 8 °C? The heat of combustion for a mole of H₂ is 242 kJ/mol.

1. 121000 J/K
2. 861 J/K
3. -861 J/K
4. -121000 J/K
5. -30.25 J/K
6. 3444 J/K
7. 30.25 J/K
8. -3444 J/K

$q_{\text{surr}} = 8 \text{ g} \cdot (2 \text{ g/mol}) \cdot (242 \text{ kJ/mol}) = 968 \text{ kJ}$

$\Delta S = q/T = 9.68 \times 10^5 \text{ J}/281 \text{ K} = 3444.84 \text{ J/K}$

24.2. A system releases 3456 J into its surroundings which are at 125 °C. By how much does this increase the entropy of the surroundings?

1. 138.24 J/K
2. 8.68 J/K
3. 11.60 J/K
4. this would decrease the entropy of the surroundings

$\Delta S = q/T = 3456 \text{ J}/398 \text{ K} = 8.68 \text{ J/K}$

25. For the vaporization of ethanol, $\Delta H_{\text{vap}} = 38.56 \text{ kJ/mol}$ and $\Delta S_{\text{vap}} = 109.7 \text{ J/mol} \cdot \text{K}$. What is the boiling point of ethanol?

1. 273.502 K
2. 0.352 K
3. 351.5 K
4. 2842 K
5. 2.84 K

$T_{\text{BP}} = \Delta H_{\text{vap}}/\Delta S_{\text{vap}} = 38.56 \times 10^3 \text{ J/mol} / 109.7 \text{ J/mol} \cdot \text{K} = 351.504 \text{ K}$

26. Your roommate left 150 g of dry ice out on the counter last night and all of it sublimated. Given that $\Delta H = 393.5 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S = 2.023 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for dry ice sublimating and that the temperature in the room was 25 °C, by how much in total has your roommate increased the entropy of the universe?

1. $-0.198 \text{ kJ}\cdot\text{K}^{-1}$
2. $0 \text{ kJ}\cdot\text{K}^{-1}$
3. $0.105 \text{ kJ}\cdot\text{K}^{-1}$
4. $0.303 \text{ kJ}\cdot\text{K}^{-1}$
5. $2.40 \text{ kJ}\cdot\text{K}^{-1}$
6. $6.89 \text{ kJ}\cdot\text{K}^{-1}$
7. $-6.00 \text{ kJ}\cdot\text{K}^{-1}$

$\Delta S_{\text{surr}} = -q/T = -\Delta H/T = -(393.5 \text{ kJ}\cdot\text{mol}^{-1})/(298 \text{ K}) = -1.320 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (at constant pressure)

$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 2.023 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} - 1.320 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 0.703 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

1 kg of dry ice = $(150 \text{ g} / 44.010 \text{ g/mol}) = 3.408 \text{ moles}$

so the total increase is $(3.408 \text{ moles}) \cdot (0.703 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = 2.40 \text{ kJ}\cdot\text{K}^{-1}$

27. Which of the following statements is always true?

1. If the number of moles of gas does not change in a chemical reaction, then $\Delta S^\circ = 0$.
2. A reaction for which ΔS° is positive is spontaneous.
3. If ΔH° and ΔS° are both positive, then ΔG° will decrease when the temperature increases.
4. An exothermic reaction is spontaneous.

$\Delta H = (+)$, $\Delta S = (+)$

$\Delta G = \Delta H - T \Delta S$

$= (+) - T (+)$

$= (+) - T$

as T increases, ΔG will decrease

28.1. What happens to CuO(s) with respect to its elements when the temperature is raised?

	S°_{m}	$\Delta H^\circ_{\text{f}}$	$\Delta G^\circ_{\text{f}}$
	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
Cu(s)	33.15		
$\text{O}_2(\text{g})$	205.14		
CuO(s)	42.63	-157.3	-129.7

The compound is

1. more stable at higher temperatures.
2. less stable at higher temperatures.
3. Unable to determine

$\Delta S^\circ_{\text{r}} = -93.09 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

28.2. A reaction for which ΔH is negative and ΔS is negative

1. could become spontaneous at low temperatures.
2. is spontaneous at any temperature.
3. could become spontaneous at high temperatures.
4. is not spontaneous at any temperature.

$\Delta G = \Delta H - T \Delta S$

To be spontaneous, ΔG must be negative. It's a good start that ΔH is negative, but if ΔS is negative, then the quantity $T \Delta S$ is also negative, and subtracting a negative ΔS is actually adding it. So for ΔG to be negative, the positive $T \Delta S$ must be a smaller number than the negative ΔH . $T \Delta S$ will be smaller at low temperatures.

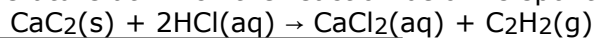
29. The standard free energy of formation of $\text{CS}_2(\ell)$ is $65.3 \text{ kJ}\cdot\text{mol}^{-1}$. This means that at 298 K

1. $\text{CS}_2(\ell)$ will not spontaneously form $\text{C(s)} + 2 \text{ S(s)}$.

2. CS₂(ℓ) is thermodynamically stable.
3. No catalyst can be found to decompose CS₂(ℓ) into its elements.
4. CS₂(ℓ) is thermodynamically unstable.
5. CS₂(ℓ) has a negative entropy.

A thermodynamically unstable compound is one which has a positive value of ΔG°_f .

30.1. Assuming that ΔH°_r and ΔS°_r are independent of temperature, what is the cutoff temperature at which the reaction below is spontaneous?



	S°_m	ΔH°_f
	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
CaC ₂ (s)	69.96	-59.8
HCl(aq)	56.5	-167.16
CaCl ₂ (aq)	59.8	-877.1
C ₂ H ₂ (g)	200.94	226.73

1. 635 K
2. 390 K
3. 573 K
4. 745 K
5. Nonspontaneous at all temperatures
6. 416 K

7. Spontaneous at all temperatures

$$\Delta S^\circ_r = 77.78 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$\Delta H^\circ_r = -256.65 \text{ kJ}\cdot\text{mol}^{-1}$$