1. On the basis of your experience, predict which of the following reactions are spontaneous.
(a) $\mathrm{NaCl}(s) \rightarrow \mathrm{NaCl}(l)$ at $25^{\circ} \mathrm{C}$
(b) $2 \mathrm{NaCl}(s) \rightarrow 2 \mathrm{Na}(s)+\mathrm{Cl}_{2}(g)$
(c) $\mathrm{CO}_{2}(s) \rightarrow \mathrm{CO}_{2}(g)$ at $25^{\circ} \mathrm{C}$
(d) $\mathrm{CO}_{2}(g) \rightarrow \mathrm{C}(s)+\mathrm{O}_{2}(g)$
(e) $\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{H}_{2} \mathrm{O}(s)$ at $25^{\circ} \mathrm{C}$
2. Without doing a calculation, predict which of the following shows a decrease in entropy?
(a) $\mathrm{CO}_{2}(s) \longrightarrow \mathrm{CO}_{2}(g)$
(b) $\mathrm{FeCl}_{2}(s)+\mathrm{H}_{2}(g) \longrightarrow \mathrm{Fe}(s)+2 \mathrm{HCl}(g)$
(c) $\mathrm{CO}(g)+2 \mathrm{H}_{2}(g) \longrightarrow \mathrm{CH}_{3} \mathrm{OH}(l)$
(d) $2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})+\longrightarrow 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
(e) $\mathrm{CH}_{3} \mathrm{OH}(l)+3 / 2 \mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(g)+\mathrm{CO}_{2}(g)$
3. The sign of $\Delta H_{\mathrm{rxn}}$ and $\Delta S_{\mathrm{rxn}}$ for several reactions are given. In which case is the reaction spontaneous at all temperatures?
(a) $\Delta H_{\mathrm{rxn}}<0 ; \Delta S_{\mathrm{rxn}}<0$
(b) $\Delta H_{\mathrm{rxn}}<0 ; \Delta S_{\mathrm{rxn}}>0$
(c) $\Delta H_{\mathrm{rxn}}>0 ; \Delta S_{\mathrm{rxn}}<0$
(d) $\Delta H_{\mathrm{rxn}}>0 ; \Delta S_{\mathrm{rxn}}>0$
(e) $\Delta H_{\mathrm{rxn}}=\Delta S_{\mathrm{rxn}}$
4. Select the correct statement that corresponds to the third law of thermodynamics.
(a) The standard Gibbs free energy change, $\Delta G^{\mathrm{o}}$, can be calculated from Gibbs free energies of formation, $\Delta G_{\mathrm{f}}{ }^{0}$
(b) The entropy of a perfect crystal of any pure substance approaches zero, as the temperature approaches absolute zero ( 0 K )
(c) The entropy change for a reaction, $\Delta S^{\circ}$, can be calculated from the standard molar entropies of the reactants and products
(d) $\Delta E_{\text {universe }}=\Delta E_{\text {system }}+\Delta E_{\text {surroundings }}=0$
(e) In any spontaneous process, $\Delta S_{\text {universe }}=\Delta S_{\text {system }}+\Delta S_{\text {surroundings }}>0$
5. Confirm that the reaction below would be spontaneous, or nonspontaneous at $25^{\circ} \mathrm{C}$, by calculating the standard free energy change, $\Delta G^{\circ}$, using values for $\Delta H^{\circ}$ and $\Delta S^{\circ}$.

$$
\begin{gathered}
\mathrm{CO}(g)+1 / 2 \mathrm{O}_{2}(g) \rightarrow \mathrm{CO}_{2}(g) \\
\Delta H_{\mathrm{rxn}}{ }^{\mathrm{o}}=-283.0 \mathrm{~kJ} ; \Delta S_{\mathrm{rxn}}{ }^{\mathrm{o}}=-86.6 \mathrm{~J} / \mathrm{K}
\end{gathered}
$$

(a) -257 kJ ; the reaction is spontaneous at $25^{\circ} \mathrm{C}$.
(b) +389 kJ ; the reaction is spontaneous at $25^{\circ} \mathrm{C}$.
(c) -389 kJ ; the reaction is spontaneous at $25^{\circ} \mathrm{C}$.
(d) +196 kJ ; the reaction is not spontaneous at $25^{\circ} \mathrm{C}$.
(e) -196 kJ ; the reaction is spontaneous at $25^{\circ} \mathrm{C}$.
6. For which of the following substances is $\Delta H_{\mathrm{f}}{ }^{\circ}=0 ; \Delta G_{\mathrm{f}}{ }^{\circ}=0$ ?
(a) $\mathrm{Al}_{2} \mathrm{O}_{3}(s)$
(b) $\mathrm{C}(s$, diamond $)$
(c) $\mathrm{CO}_{2}(g)$
(d) $\mathrm{Cl}_{2}(\mathrm{~g})$
(e) $\mathrm{MgCO}_{3}(\mathrm{aq})$
7. When magnesium sulfite decomposes, the solid transforms into magnesium oxide and sulfur dioxide.

$$
\mathrm{MgSO}_{3}(s) \rightarrow \mathrm{MgO}(s)+\mathrm{SO}_{2}(g)
$$

At what temperature will this reaction be spontaneous according to Gibb's Energy?
$\Delta H_{\mathrm{f}}{ }^{\mathrm{o}}$ in $\mathrm{kJ} / \mathrm{mol}$ for: $\mathrm{MgSO}_{3}(s)=-1068, \mathrm{MgO}(s)=-601.8, \mathrm{SO}_{2}(g)=-296.8$
$\mathrm{S}^{\mathrm{o}}$ in $\mathrm{J} / \mathrm{mol} \mathrm{K}$ for: $\mathrm{MgSO}_{3}(s)=121, \mathrm{MgO}(s)=27, \mathrm{SO}_{2}(g)=248.1$
(a) temps below -63.1 K
(b) temps below 179.5 K
(c) temps below 415.8 K
(d) temps above 415.8 K
(e) temps above 1100 K
8. Confirm that the reaction below would be spontaneous, or nonspontaneous at $25^{\circ} \mathrm{C}$, by calculating the standard free energy change, $\Delta G^{0}$, using values for $\Delta G_{\mathrm{f}}{ }^{\mathrm{o}}$.

$$
2 \mathrm{C}_{4} \mathrm{H}_{10}(g)+13 \mathrm{O}_{2}(g) \rightarrow 8 \mathrm{CO}_{2}(g)+10 \mathrm{H}_{2} \mathrm{O}(l)
$$

$\begin{array}{lllll}\Delta G_{\mathrm{f}}{ }^{\mathrm{o}}(\mathrm{kJ} / \mathrm{mol}) & -15.71 & 0 & -394.4 & -237.2\end{array}$
(a) -615.89 kJ ; the reaction is spontaneous.
(b) +615.89 kJ ; the reaction is not spontaneous.
(c) 0 kJ ; the reaction is spontaneous.
(d) +5496 kJ ; the reaction is not spontaneous.
(e) -5496 kJ ; the reaction is spontaneous.
9. If a 5.0 L flask holds 0.125 moles of nitrogen at STP, what happens to the entropy of the system upon cooling the gas to $-75^{\circ} \mathrm{C}$ ?
(a) The entropy is zero.
(b) The entropy increases.
(c) The entropy remains the same.
(d) The entropy decreases.
(e) There is too little information to assess the change.

10 . In the first 10.0 s of the reaction, the concentration of B decreased from 0.50 M to 0.37 M . What is the rate of the reaction in this time interval?

$$
2 \mathrm{~A}+3 \mathrm{~B} \rightarrow 2 \mathrm{C}+\mathrm{D}
$$

(a) $2.3 \mathrm{M} / \mathrm{s}$
(b) $0.50 \mathrm{M} / \mathrm{s}$
(c) $0.13 \mathrm{M} / \mathrm{s}$
(d) $1.3 \times 10^{-2} \mathrm{M} / \mathrm{s}$
(e) $4.3 \times 10^{-3} \mathrm{M} / \mathrm{s}$
11. If ammonia, $\mathrm{NH}_{3}(\mathrm{~g})$, is being produced at a rate of $6.29 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$, at what rate is nitrogen gas being consumed?

$$
\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightarrow 2 \mathrm{NH}_{3}(g)
$$

(a) $9.44 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$.
(b) $6.29 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$.
(c) $4.17 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$.
(d) $3.15 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$
(e) $1.26 \times 10^{-4} \mathrm{M} / \mathrm{s}$
12. Based on the generic rate law, which of the following is not really correct?

$$
\text { Rate of reaction }=k[\mathrm{~A}]^{m}[\mathrm{~B}]^{n}
$$

(a) The experimentally determined exponents $(m, n)$ are referred to as the order of the reaction with respect to A and B , respectively.
(b) If $m=1$, the reaction is first order with respect to A .
(c) If $m=0$, the reaction is independent of the concentration of A .
(d) If $n=2$, the reaction is second order with respect to $B$.
(e) The overall order of the reaction $=\mathrm{m} \times \mathrm{n}$
13. Consider the reaction: $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}$, and a kinetics study on this reaction yielded:

| $[\mathrm{A}] \mathrm{mol} \cdot \mathrm{L}^{-1}$ | $[\mathrm{~B}] \mathrm{mol} \cdot \mathrm{L}^{-1}$ | Rate $=\mathrm{mol} \cdot \mathrm{L}^{-1} \cdot \mathrm{~s}^{-1}$ |
| :--- | :--- | :--- |
| 0.100 | 0.200 | $4.45 \times 10^{-3}$ |
| 0.050 | 0.200 | $1.12 \times 10^{-3}$ |
| 0.050 | 0.100 | $1.11 \times 10^{-3}$ |

What is the value of the rate constant?
(a) $3.20 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}$
(b) $19.8 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}$
(c) $0.445 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}$
(d) $4.60 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}$
(e) $4.60 \mathrm{~s}^{-1}$
14. The decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ in solution of carbon tetrachloride is a first-order reaction:

$$
2 \mathrm{~N}_{2} \mathrm{O}_{5} \rightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}
$$

The rate constant at a given temperature is found to be $4.50 \times 10^{-4} \mathrm{~s}^{-1}$. If the initial concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ is 0.250 M , what is its concentration after exactly 15 minutes have passed?
(a) 0.000 M
(b) 0.073 M
(c) 0.167 M
(d) 0.195 M
(e) 0.199 M
15. Consider the production of oxygen from ozone. The mechanism includes two elementary steps:

$$
\begin{gathered}
\mathrm{O}_{3}+\mathrm{Cl} \cdot \rightarrow \mathrm{ClO}+\mathrm{O}_{2} \\
\mathrm{ClO}+\mathrm{O}_{3} \rightarrow \mathrm{Cl} \cdot+2 \mathrm{O}_{2}
\end{gathered}
$$

Which species is a reactive intermediate?
(a) $\mathrm{O}_{3}$
(b) ClO -
(c) $\mathrm{Cl} \cdot$
(d) $\mathrm{O}_{2}$
(e) both ClO and Cl -
16. If a reaction is second order with respect to $[B]$, doubling the concentration of $[B]$ will result in:
(a) a doubling of the rate
(b) a tripling of the rate
(c) a four-fold increase in rate
(d) an eight-fold increase in rate
(e) no change in the rate of reaction
17. If the initial concentration of the reactant in a first-order reaction $A \rightarrow$ products is $0.64 \mathrm{~mol} / \mathrm{L}$ and the half-life is 30.0 s , how long would it take for the concentration of the reactant to drop to $0.040 \mathrm{~mol} / \mathrm{L}$ ?
(a) 30.0 s
(b) 60.0 s
(c) 90.0 s
(d) 120.0 s
(e) 150.0 s
18. Consider the elementary step: $2 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{C}$. What type of elementary step is this?
(a) unimolecular
(b) bimolecular
(c) termolecular
(d) all of the above
(e) none of the above
19. Raising the temperature of a reaction elevates the rate of reaction by:
(a) increasing the energy of activation
(b) creating more molecules in the reaction.
(c) providing a new reaction mechanism
(d) increasing the number of molecules moving at a speed sufficiently high enough to produce a reactive collision.
(e) decreasing the entropy of the system.
20. Which statement is true regarding the sublimation of dry ice $\left(\operatorname{solid} \mathrm{CO}_{2}\right)$ at $25^{\circ} \mathrm{C}$ ?
a) $\Delta \mathrm{H}$ is positive; $\Delta \mathrm{S}$ is positive; $\Delta \mathrm{G}$ is positive.
b) $\Delta \mathrm{H}$ is positive; $\Delta \mathrm{S}$ is positive; $\Delta \mathrm{G}$ is negative.
c) $\Delta \mathrm{H}$ is negative; $\Delta \mathrm{S}$ is positive; $\Delta \mathrm{G}$ is negative.
d) $\Delta \mathrm{H}$ is positive; $\Delta \mathrm{S}$ is negative; $\Delta \mathrm{G}$ is positive.
e) $\Delta \mathrm{H}$ is negative; $\Delta \mathrm{S}$ is negative; $\Delta \mathrm{G}$ is negative.

Answers:
1 (c), 2 (c), 3 (b), 4 (b), 5 (a), 6 (d), 7 (e), 8 (e), 9 (d), 10 (e), 11 (d), 12 (e), 13 (c), 14 (c), 15 (b), 16 (c), 17 (d), 18 (c), 19 (d), 20 (b)

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## SOME USEFUL CONSTANTS

| (a more complete list appears in Appendix B) |  |
| :---: | :---: |
| Atomic mass unit | $1 \mathrm{amu}=1.6606 \times 10^{-24} \mathrm{~g}$ |
| Avogadro's number | $N=6.02214179 \times 10^{23}$ particles $/ \mathrm{mol}$ |
| Electronic charge | $e=1.60218 \times 10^{-19}$ coulombs |
| Faraday constant | $F=96,485.3399$ coulombs $/ \mathrm{mol} e^{-}$ |
| Gas constant | $R=0.08206 \frac{\mathrm{~L} \mathrm{~atm}}{\mathrm{~mol} \mathrm{~K}}=1.987 \frac{\mathrm{cal}}{\mathrm{~mol} \mathrm{~K}}$ |
|  | $=8.314472 \frac{\mathrm{~J}}{\mathrm{~mol} \mathrm{~K}}=8.314472 \frac{\mathrm{kPa} \mathrm{dm}^{3}}{\mathrm{~mol} \mathrm{~K}}$ |
| Pi | $\pi=3.1415927$ |
| Planck's constant | $b=6.62606896 \times 10^{-34} \mathrm{~J} \mathrm{~s}$ |
| Speed of light (in vacuum) | $c=2.99792458 \times 10^{8} \mathrm{~m} / \mathrm{s}$ |

## SOME USEFUL RELATIONSHIPS

| Mass and Weight | Length |
| :---: | :---: |
| SI Base Unit: Kilogram (kg) | SI Base Unit: Meter (m) |
| 1 kilogram $=1000$ grams $=2.205$ pounds | 1 inch $=2.54$ centimeters (exactly) |
| 1 gram $=1000$ milligrams | 1 meter $=100$ centimeters $=39.37$ inches |
| 1 pound $=453.59$ grams | 1 yard $=0.9144$ meter |
| $1 \mathrm{amu}=1.6606 \times 10^{-24}$ grams | 1 mile $=1.609$ kilometers |
| $1 \mathrm{gram}=6.022 \times 10^{23} \mathrm{amu}$ | 1 kilometer $=1000$ meters $=0.6215$ mile |
| 1 ton $=2000$ pounds | 1 Ångstrom $=1.0 \times 1.0^{-10}$ meters $=1.0 \times 10^{-8}$ centimeters |
| Volume | Energy |
| SI Base Unit: Cubic Meter ( $\mathrm{m}^{3}$ ) | SI Base Unit: Joule (J) |
| 1 liter $=0.001$ cubic meter <br> 1 liter $=1000$ cubic centimeters $=1000 \mathrm{~mL}$ | 1 calorie $=\underset{\mathrm{kg} \mathrm{m}^{2}}{4.184 \text { joules }}=4.129 \times 10^{-2} \mathrm{~L}$ atm |
| 1 liter $=1.056$ quarts | $1 \text { joule }=1 \frac{\mathrm{~kg} \mathrm{~m}^{2}}{2^{2}}=0.23901 \text { calorie }$ |
| 1 quart $=0.9463$ liter |  |
| 1 milliliter $=0.001$ liter $=1$ cubic centimeter cubic foot $=7.475$ gallons $=28.316$ liters | $\begin{aligned} 1 \text { joule } & =1 \times 10^{7} \text { ergs } \\ 1 \text { electron volt } & =1.6022 \times 10^{-19} \text { joule } \end{aligned}$ |
| 1 gallon $=4$ quarts | 1 electron volt $=96.485 \mathrm{~kJ} / \mathrm{mol}$ |
|  | $1 \mathrm{~L} \mathrm{~atm}=24.217$ calories $=101.325$ joules |
| Pressure | Temperature |
| SI Base Unit: Pascal (Pa) | SI Base Unit: Kelvin (K) |
| 1 pascal $=\frac{\mathrm{kg}}{}$ | $0 \mathrm{~K}=-273.15^{\circ} \mathrm{C}$ |
| 1 pascal $=\frac{}{\mathrm{ms}^{2}}=1$ Newton $/ \mathrm{m}$ | $\mathrm{K}={ }^{\circ} \mathrm{C}+273.15^{\circ}$ |
| $1 \mathrm{atmosphere}=760$ torr | ${ }^{\circ} \mathrm{F}=1.8\left({ }^{\circ} \mathrm{C}\right)+32^{\circ}$ |
| $=760$ millimeters of mercury | ${ }^{\circ} \mathrm{C}={ }^{\circ} \mathrm{F}-32^{\circ}$ |
| $=1.01325 \times 10^{5}$ pascals | $1.8{ }^{\circ}$ |
| $=1.01325 \mathrm{bar}$ $=14.70$ pounds per square inch |  |
| 1 torr $=1$ millimeter of mercury |  |

