## Answers to Exercise 12.2

## $K_{a}, p K_{a}, K_{b}$ and $p K_{a}$

1. 

(a) Start with the initial equation:

$$
K_{a} \cdot K_{b}=K_{w}
$$

Take the logarithm of both sides and multiply both sides by -1 :

$$
-\log \left(K_{a} \cdot K_{b}\right)=-\log \left(K_{w}\right)
$$

Recognize that the $\log (a \times b)=\log (a)+\log (b)$ :

$$
-\left[\log \left(K_{a}\right)+\log \left(K_{b}\right)\right]=-\log \left(K_{w}\right)
$$

Break open the brackets on the left side of the equation:

$$
-\log \left(K_{a}\right)+\left[-\log \left(K_{b}\right)\right]=-\log \left(K_{w}\right)
$$

Use $p$ Anything $=-\log ($ Anything $)$ to convert each term into $p$ Something:

$$
p K_{a}+p K_{b}=p K_{w}
$$

Finally, $p K_{w}=-\log \left(K_{w}\right)$ and $K_{w}=10^{-14}$ at $25^{\circ} \mathrm{C}$.
So, $p K_{w}=-\log \left(10^{-14}\right)=-(-14)=14$ at $25^{\circ} \mathrm{C}$.
Therefore, $p K_{a}+p K_{b}=14$ at $25^{\circ} \mathrm{C}$.
(b) $\quad p K_{a}=-\log \left(K_{a}\right)$ therefore $K_{a}=10^{-p K_{a}}$

For formic acid, $K_{a}=10^{-3.74}=1.8 \times 10^{-4}$
(c)


formic acid

$$
K_{a}=1.8 \times 10^{-4}
$$

$$
p K_{a}=3.74
$$

formate

$$
K_{b}=5.5 \times 10^{-11}
$$

$$
p K_{b}=10.26
$$

(d) The simplest approach is to calculate $p K_{b}$ first then use it to calculate $K_{b}$.

At $25^{\circ} \mathrm{C}, p K_{a}($ conj. acid $)+p K_{b}($ conj. base $)=14$.
Therefore, $p K_{b}$ (conj.base) $=14-p K_{a}($ conj.acid $)$
Therefore, $p K_{b}($ formate $)=14-p K_{a}($ formic acid $)=14-3.74=10.26$
$p K_{b}=-\log \left(K_{b}\right)$ therefore $K_{b}=10^{-p K_{b}}$
For formic acid, $K_{a}=10^{-10.26}=5.5 \times 10^{-11}$
2.

| Relative Strength | $\boldsymbol{p} \boldsymbol{K}_{\boldsymbol{a}}$ | $\boldsymbol{K}_{\boldsymbol{a}}$ | Acid |
| :--- | :---: | :---: | :---: |
| Strong | 7 | $1 \times 10^{7}$ <br> $(10,000,000)$ | HCl |
| Border between strong and weak | 0 | 1 | $\mathrm{H}_{3} \mathrm{O}^{+}$ |
| Weak | 2.1 | $10^{-2.1}=0.008$ | $\mathrm{H}_{3} \mathrm{PO}_{4}$ |
| Very weak | 14 | $1 \times 10^{-14}$ <br> $(0.0000000000001)$ | $\mathrm{H}_{2} \mathrm{O}$ |
| So weak we don't call it an acid | 48 | $1 \times 10^{-48}$ | $\mathrm{CH}_{4}$ |

3. 

(a) Look up the $p K_{a}$ values for both $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$. Whichever species has a lower $p K_{a}$ value is the stronger acid.
or
Look up the $\mathrm{K}_{a}$ values for both $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$. Whichever species has a higher $K_{a}$ value is the stronger acid.
(b) Look up the $p K_{a}$ values for both $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH}_{2}^{+}$and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}_{2}^{+}$. Whichever species has a higher $p K_{a}$ value is the weaker acid and therefore has the stronger conjugate base.
or
Look up the $K_{a}$ values for both $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH}_{2}^{+}$and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}_{2}^{+}$. Whichever species has a lower $K_{a}$ value is the weaker acid and therefore has the stronger conjugate base.

It is important to note that it is the $K_{a}$ (or $p K_{a}$ ) value for a base's conjugate acid that is relevant for part (b) NOT the $K_{a}$ (or $p K_{a}$ ) value for the base itself!
If you want to compare properties of the bases themselves, compare $K_{b}$ (or $p K_{b}$ ) values. A stronger base has a larger $K_{b}$ or a smaller $p K_{b}$.

