Let $\{|v_i\rangle\}$ be the basis for V space
& $\{|w_i\rangle\}$ be the basis for W space

If we take the tensor product space $K = V \otimes W$, then the basis for such a space is $\{|v_i\rangle \otimes |w_j\rangle\}$

Now, the statement which I initially assumed was any general vector in K space can be written as the tensor product of any two vectors $|v\rangle$ & $|w\rangle$ in the space V & W respectively. Let's see if the above made statement is correct:

Let,

$$|v\rangle = \sum_i a_i |v_i\rangle$$

$$|w\rangle = \sum_i b_i |w_i\rangle$$

$$|k\rangle = |v\rangle \otimes |w\rangle = \sum_{i,j} a_i b_j |v_i\rangle \otimes |w_j\rangle \quad \text{— (I)}$$

But we know that the basis for K space is the set $\{|v_i\rangle \otimes |w_j\rangle\}$.

Let's now write the vector $|k\rangle$ in this basis

$$|k\rangle = \sum_{i,j} c_{ij} |v_i\rangle \otimes |w_j\rangle \quad \text{— (II)}$$

But with only a little thought we can see that (II) & (I) are not always equivalent. Suppose we take the vector,

$$|k\rangle = \frac{1}{\sqrt{2}} |v_1\rangle \otimes |w_1\rangle + \frac{1}{\sqrt{2}} |v_2\rangle \otimes |w_2\rangle$$

then we can never have any vector $|v\rangle$ & $|w\rangle$ such that,

$$|k\rangle = |v\rangle \otimes |w\rangle$$

Hence, eq^n (I) is wrong for writing general $|k\rangle$.

Ex: $$|\psi\rangle = \frac{|00\rangle + |11\rangle}{\sqrt{2}}$$

Note that this part of the K space where we cannot reach using $|v\rangle \otimes |w\rangle$ contains all the entangled state.

$\therefore$ Hallmark of entanglement,

$$|\psi\rangle \neq |v\rangle \otimes |w\rangle$$

So, to answer your question, we use eq^n (II) for general $|k\rangle$ hence use c_{ij}.