EQUILIBRIUM CONCENTRATIONS AFTER COMPRESSION OF A GASEOUS SYSTEM CANNOT BE LESS THAN BEFORE COMPRESSION

A common student error is perpetuated in Figure 15.13 of Brown, LeMay & Bursten's *Chemsistry the Central Science* 11th edition, page 650 in my annotated instructor's edition. It is suggested that after compression of a mixture of NO_2 and N_2O_4 gases, the colour of the mixture is lighter than at the beginning. Of course, this cannot be so, regardless of the equilibrium. The concentration of all substances present at equilibrium must be increased by an increase in pressure, and return to equilibrium cannot reduce the concentration to a value lower than that before compression. Similar arguments may be applied to substances in solution.

The proposition may be proved as follows:
Consider an equilibrium mixture of reactants A & B and products D & E.

$$a\mathrm{A(g)} + b\mathrm{B(g)} \rightleftharpoons d\mathrm{D(g)} + e\mathrm{E(g)}$$

For simplicity we use these same symbols, *A, B, D, & E* (italicised) to represent their initial equilibrium concentrations. i.e.
The initial, equilibrium concentration of A = A,
The initial, equilibrium concentration of B = B,
The initial, equilibrium concentration of D = D,
The initial, equilibrium concentration of E = E.

Thus
$$K = \frac{D^d E^e}{A^a B^b}$$
or
$$KA^a B^b = D^d E^e \quad - (1)$$

If the mixture is compressed, then each concentration is multiplied by the same factor, α. Hence the new, non-equilibrium concentrations of the species are: αA, αB, αD and αE respectively.
We now construct the "ICE" table:

	aA(g)	+	bB(g)	⇌	dD(g)	+	eE(g)
Initial /M	αA		αB		αD		αE
Change /M	$-ax$		$-bx$		$+dx$		$+ex$
Equilibrium /M	$\alpha A-ax$		$\alpha B-bx$		$\alpha D+dx$		$\alpha E+ex$

We may now write:

$$K = \frac{(\alpha D + dx)^d (\alpha E + ex)^e}{(\alpha A - ax)^a (\alpha B - bx)^b}$$

$$\text{or } K(\alpha A - ax)^a (\alpha B - bx)^b = (\alpha D + dx)^d (\alpha E + ex)^e \quad - (2)$$

Dividing (2) by (1) gives:

$$\frac{(\alpha A - ax)^a (\alpha B - bx)^b}{A^a B^b} = \frac{(\alpha D + dx)^d (\alpha E + ex)^e}{D^d E^e}$$

$$\therefore \left(\frac{\alpha A - ax}{A}\right)^a \left(\frac{\alpha B - bx}{B}\right)^b = \left(\frac{\alpha D + dx}{D}\right)^d \left(\frac{\alpha E + ex}{E}\right)^e$$

$$\therefore \left(\alpha - \frac{a}{A}x\right)^a \left(\alpha - \frac{b}{B}x\right)^b = \left(\alpha + \frac{d}{D}x\right)^d \left(\alpha + \frac{e}{E}x\right)^e \quad -(3)$$

where each term of equation (3) inside the brackets represents the final equilibrium concentration of a reactant or product divided by its initial equilibrium concentration. We now have 3 cases to consider:

x>0

Note that α >1 and *a, b, d, e, A, B, C, & D* >0
Each of the terms of the RHS of equation (3) is clearly greater than 1, and so the final equilibrium concentrations of the products exceed their initial equilibrium concentrations.

The product of two terms greater than 1 must also be greater than 1 and so the RHS of (3) is greater than 1. Consequently, the LHS of equation (3) is also greater than 1:

$$\left(\alpha - \frac{a}{A}x\right)^{a}\left(\alpha - \frac{b}{B}x\right)^{b} > 1 \quad \text{- (4)}$$

for all physically plausible values of *a, b, A & B*.
If one term on the LHS of equation (4) were less than unity, since there is no restriction on the values of *a, b, A, & B*, except that all are greater than zero, then both terms could be less than unity, violating the inequality. Hence both terms must be greater than unity. Consequently, the final equilibrium concentrations of the reactants exceed their initial equilibrium concentrations.

x<0

Now the situation of equation (3) is reversed but the argument works as before. The LHS of equation (3) must be greater than one, and so, therefore must the RHS, and all the terms inside the brackets. Hence the final equilibrium concentrations of both products and reactants exceed their initial equilibrium concentrations.

x=0

In this case the final equilibrium concentrations are αA, αB, αD, & αE, and since $\alpha > 1$, these concentrations are all greater than the initial equilibrium concentrations.

- We note that the argument may easily be extended to any number of reactants and products.

- To summarise, after compression, the equilibrium concentration of each product and each reactant is greater than it was before compression.

- We also note that the argument may easily be extended to removal of solvent from a solution, since this is equivalent to compression.

- A further extension applies to decompression and dilution. Here $\alpha < 1$. The argument is turned on its head to show that the equilibrium concentration of each product and each reactant is less than before the decompression or dilution.

ADDITION OF A REACTANT OR PRODUCT TO A SYSTEM AT EQUILIBRIUM CANNOT LEAD TO A LOWER CONCENTRATION OF THAT SUBSTANCE ONCE EQUILBRIUM IS RESTORED.

The argument is similar to the previous one, except that just one species, for example A, is multiplied by a factor α, where $\alpha > 1$.
The ICE table now becomes:

	aA(g)	+	bB(g)	⇌	dD(g)	+	eE(g)
Initial /M	αA		B		D		E
Change /M	$-ax$		$-bx$		$+dx$		$+ex$
Equilibrium /M	$A-ax$		$B-bx$		$D+dx$		$E+ex$

and so,

$$K = \frac{(D+dx)^{d}(E+ex)^{e}}{(\alpha A-ax)^{a}(B-bx)^{b}}$$

$$\text{or } K(\alpha A-ax)^{a}(B-bx)^{b} = (D+dx)^{d}(E+ex)^{e} \quad \text{- (5)}$$

Dividing (5) by (1) gives:

$$\frac{(\alpha A-ax)^a(B-bx)^b}{A^aB^b}=\frac{(D+dx)^d(E+ex)^e}{D^dE^e}$$

$$\therefore\left(\frac{\alpha A-ax}{A}\right)^a\left(\frac{B-bx}{B}\right)^b=\left(\frac{D+dx}{D}\right)^d\left(\frac{E+ex}{E}\right)^e$$

$$\therefore\left(\alpha-\frac{a}{A}x\right)^a\left(1-\frac{b}{B}x\right)^b=\left(1+\frac{d}{D}x\right)^d\left(1+\frac{e}{E}x\right)^e \quad -(6)$$

x>0

Clearly the RHS of (6) is greater than unity, and hence the LHS must be. The term $\left(1-\frac{b}{B}x\right)^b$ is less than unity, and hence the other term, $\left(\alpha-\frac{a}{A}x\right)^a$ must be greater than unity. Since this represents the final equilibrium concentration of reactant A divided by the original equilibrium concentration of reactant A, the final equilibrium concentration of A must be greater than its initial concentration.

x<0

The term $\left(\alpha-\frac{a}{A}x\right)^a$ is immediately seen to be greater than unity. *QED*.

x=0

Now $\left(\alpha-\frac{a}{A}x\right)^a=\alpha>1$. *QED.*

- As previously, the argument may readily be extended to any number of reactants and products.
- To summarise, after addition of reactant, the equilibrium concentration of the reactant is greater than before compression.
- The argument applies equally well to the addition of product, since in an equilibrium there is no real distinction between reactants and products.
- A further extension applies to removal of reactant or product. Here $\alpha < 1$. The argument is turned on its head to show that the equilibrium concentration of each product and each reactant is less than before the removal.