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MATEMATIKA KIMIA
Lampiran – Konsep pendekatan Stirling

(Sumber : Barrante, Applied Mathematics fo Physical Chemistry)

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Konsep pendekatan Stirling

Throughout many areas of physical chemistry, and particularly in the area of statistical mechanics, factorials are used extensively. One will recall that N factorial, written $N!$, is defined as

$$N! = (1)(2)(3)\cdots(N-1)(N) \qquad \text{(IV-1)}$$

where $0! = 1$ and $1! = 1$.

Let us consider, now, an expression for the natural logarithm of $N!$.

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \cdots + \ln N$$

$$\ln N! = \sum_{x=1}^{N} \ln x \qquad \text{(IV-2)}$$

If N is very large, however, this summation can be replaced by the integral

$$\ln N! \cong \int_1^N \ln x \, dx \qquad \text{(IV-3)}$$

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which, when integrated by parts, gives

$$\ln N! \cong x \ln x - x \Big|_1^N = N \ln N - N + 1 \qquad \text{(IV-4)}$$

However, if N is much larger than 1, we can write

$$\ln N! \cong N \ln N - N \quad \text{for large } N \qquad \text{(IV-5)}$$

Equation (IV-5) is known as *Stirling's approximation* and can be used to approximate ln $N!$ when N is a very large number.

A much more accurate expression for approximating $N!$, particularly for nonintegral values of N, can be found using gamma functions. This approach, which is beyond the scope of this text, leads to *Stirling's formula*

$$N! = \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \qquad \text{(IV-6)}$$

which again is valid as N becomes very large. Taking the logarithm of this equation gives

$$\ln N! \cong N \ln N - N + \frac{1}{2} \ln (2\pi N) \quad \text{for large } N \qquad \text{(IV-7)}$$

Equation (IV-6) gives better results for smaller values of N.

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Let us compare the abilities of Equations (IV-4), (IV-5), and (IV-6) to approximate a relatively small number for N: 60!. The actual value is 8.32×10^{81}. Equation (IV-4) gives a value for $60! = 1.16 \times 10^{81}$. Equation (IV-5) gives an even poorer approximation for $60! = 4.27 \times 10^{80}$. Equation (IV-6) gives a value for $60! = 8.31 \times 10^{81}$. Clearly, for an N value as small as 60, Equation (IV-6) gives the best results. As N gets much larger, however, all three equations work better and better. In chemical statistics, where N usually represents the number of molecules in a macroscopic system, 10^{23}, all equations reduce to Equation (IV-5).