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eco-chem

Questions

Q184. Over a range of about $\pm 3^\circ\text{C}$ from normal body temperature the metabolic rate, M_T , is given by: $M_T = M_{37}(1.1)^{\Delta T}$, where M_{37} is the normal rate and ΔT is the change in T . Discuss this equation in terms of a possible molecular interpretation.

Q185. In Cleveland, Ohio a tank of liquefied natural gas (LNG) ruptured in 1944 and resulted in a fire which killed 128 people. It was suggested that, "LNG vapors are heavier than air and will accumulate in layers." Evaluate this statement.

Q186. Excessive sweating or hookworm infection may cause a disease, only in human males, in Egypt and Iran characterized by slow growth but rapidly cured by adding zinc to the diet. Suggest a possible molecular mechanism which requires zinc.

Q187. The free amino-acid nitrogen content of blood plasma is normally about 5 mg/100 ml. Tissues in which protein synthesis occurs contain 5–10 times this concentration. Do these facts necessarily mean that work must be expended for net entrance of amino acids into tissues?

This column consists of questions (plus possible, but certainly not uniquely satisfactory, answers) requiring no more than a concurrent first-year, college level course, a data handbook, and a willingness to apply fundamental chemical ideas to the systems which surround us (or even are inside us). Contributions for possible inclusion are solicited. Initiated in the January, 1972, issue of *this Journal*.

Answers

A184. $M_T = M_{37}(1.1)^{\Delta T} = M_{37}(1.1)^{T - 37}$, where $T = ^\circ\text{C}$ body temperature, and M 's are rates at T and at 37°C . The Arrhenius equation is $k = Ae^{-\Delta H^\ddagger/RT}$ or $k_2/k_1 = e^{-(\Delta H^\ddagger/R)(1/T_2 - 1/T_1)} = e^{-(\Delta H^\ddagger/R)(T_1 - T_2)/(T_1T_2)}$, where the T 's are $^\circ\text{K}$.

But T_1T_2 is approximately constant over this range, so we can write

$$k_2/k_1 = e^{-(\Delta H^\ddagger/RT^2)(T_1 - T_2)} = \text{const}^{(T_2 - T_1)} = \text{const}^{\Delta T}$$

Now ΔT can be either in Kelvins or in degrees Celsius, and the ratio of the k 's is the same as the ratios of the rates of reaction at the two temperatures. This equation has the same form as that in the problem. It is the same equation as $e^{\Delta H^\ddagger/RT^2} = 1.1$. Since $R = 1.99 \text{ cal/mole}^\circ\text{K}$ and $T = 310^\circ\text{K}$ we get $\Delta H^\ddagger = 18,000 \text{ cal/mole}$. This is consistent with a single rate determining step which controls metabolic rate within $\pm 3^\circ$ of 37°C . This is only reasonable in a normal steady state. Stresses will bring different steps into the determination of the rate. Note that ΔH^\ddagger is not very large so that a change in T does not have a great effect on metabolic rate.

A185. The m.w. of CH_4 is 16, of air 29. At the same T and P air is 1.8 times as dense as CH_4 , so that a cloud of CH_4 would rise rapidly in air as shown by its use in filling balloons. If the air temperature is 300°K , CH_4 gas would have to be at $(16/29)300 \approx 160^\circ\text{K}$ to have the same density as air. The b.p. of CH_4 is 120°K , and the density of gaseous CH_4 at 120°K is $160/120 = 1.3$ times that of air at 300°K . Thus dense clouds of very cold CH_4 gas could be "heavier" than air. However, the presence of

such cold gas would cause condensation of water vapor with local warming. This warming, plus the turbulence accompanying vaporization should minimize the formation of dense pockets of CH_4 . Rapid mixing (matter of minutes) would be expected to dilute the gas below its flammability limits in air. [W. W. Crouch and J. C. Hillyer, *Chem Tech*, (April 21, 1972)]

The explosion probably resulted either from a spark at the point of rupture, or from the cold ($<160^\circ\text{K}$) gas flowing quickly to an open flame or spark.

A186. Biological systems contain mainly H, C, O, N, P, and S. Zn^{2+} forms ZnS , rather insoluble in water, but ZnS bonds are nowhere near as apt to form as are S bonds with most of the p elements (e.g., Cu, Hg, Ag, Pb, etc.). A possibility is that Zn^{2+} breaks up a critical sulfur bond in the biological poison and so inactivates it. Zn^{2+} also forms moderately strong bonds to $:\text{NH}_2$, $:\text{O}-\text{H}$, and $:\text{O}-\text{C}$ so there are many possible modes of action. Or Zn may be required in minute amounts which are reduced by sweating or hookworm infection. Adding Zn to the diet corrects the deficiency.

A187. Work must always be done ($\Delta G = +$, for the system) to move molecules against a concentration gradient. Thus, if "free amino-acid nitrogen content" is used in the same sense in the plasma and in the tissue, work must be done. But, if the amino acids are complexed more in the tissue (or otherwise have a net lower chemical potential) than in plasma then transfer by diffusion, without net work being done ($\Delta G = -$), may take the amino acids from the plasma to the synthetic sites in the tissue.