# Entropy Is Simple, Qualitatively

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Qualitatively, entropy is simple. What it is, why it is so useful in understanding the behavior of macro systems or of molecular systems is easy to state. The key to simplicity has been mentioned by chemists and physicists.[1] In classical thermodynamics, it is viewing entropy increase as a measure of the dispersal of energy from localized to spread out (as in the examples of the next section). In "molecular thermodynamics" it is considering the change in systems from having fewer accessible microstates to having many more accessible microstates (as described in later sections). Most important to educators, emphasizing energy dispersal can provide a direct relationship of molecular behavior to entropy change, an idea that can be readily understood by beginning college students.

This view was broached partially in previous articles that showed "disorder" was outmoded and misleading as a descriptor for entropy *(1, 2)*. The present article substantiates the power of seeing entropy as the "spreading and sharing" of energy (theoretically established by Leff *[3a]*) in classical and molecular thermodynamics in important equilibrium situations and chemical processes.

The preceding introduction in no way denies the subtlety or the difficulty of many aspects of thermodynamics involving entropy. In numerous cases the theory or calculation or experimental determination of entropy change can be overwhelming even to graduate students and challenging to experts. In complex cases, the qualitative relation of energy dispersal to entropy change can be so inextricably obscured that it is moot. However, this does not weaken its explanatory power in the common thermodynamic examples presented to beginning students, nor in using energy dispersal to introduce them to spontaneous change in chemistry.

## An Overview: What Entropy Change Is

### The Dispersal of Energy[2]

A hot pan spontaneously disperses some of its energy to the cooler air of a room. Conversely, even a cool room would disperse a portion of its energy to colder ice cubes placed in it. When a container of nitroglycerine is merely dropped on the floor, the nitroglycerine may change into other substances explosively, because some of its internal bond energy is spread out in increasing the vigorous motions of the molecules in the gaseous products. At a high pressure in a car tire, the compressed air tends to blow out and dissipate its more concentrated energy to the lower pressure atmosphere. At any pressure, ideal gases will spontaneously flow into an evacuated chamber, spreading the energy of their molecular motions over the final larger volume. Hydrogen and oxygen in a closed chamber will remain unchanged for years and probably for millennia, despite their greater combined internal

bond energies compared to water, yet they will react explosively to dissipate some of that internal energy in forming the lower energy water if a spark is introduced.

In these six varied examples, and in all everyday spontaneous physical happenings and chemical reactions, some type of energy flows from being localized or concentrated to becoming spread out to a larger space. This common language summary will be given precise descriptions in thermodynamics and in molecular behavior later.

In most spontaneous chemical reactions the products that are formed have lower potential energies than the starting materials. Thus, as a result of such a reaction, some of the reactants' bond energy is dispersed to cause increased molecular motion in the products. Less common at room temperatures (but routine in blast furnace conditions) are endothermic reactions. In this kind of reaction, substances (alone or with others) react so that energy from the *more-concentrated-energy* surroundings is dispersed to the bonds and motions of the molecules of the *less-concentrated-energy* substances in a system. The result is the formation of new substances with higher potential energies than their starting materials.

Parallel with the behavior of energy in chemical phenomena is its dispersal in all spontaneous physical events, whether they are complex and exotic, or as simple and too common as a car collision.[2]

### Entropy Change: The Index of Energy Dispersal

Clausius' definition of entropy change, $dS = dq_{rev}/T$, could be expressed verbally as "entropy change = quantity of energy dispersed at a temperature $T$". Clausius' synonym for entropy was *Verwandlung*, transformation. This definition does not imply that entropy is "disorder", nor that it is a measure of "disorder", nor that entropy is a driving force. Instead, the reason for transformation in classical thermodynamics is energy's dissipating, dispersing, spreading out from where it is confined in a small space to a larger volume whenever it is not restricted from doing so. Entropy is the measure or the index of energy dispersal at a temperature $T$.

### The Molecular Basis for Understanding Simple Entropy Change (3a, 4)

The difference between Figure 1A and B is *symbolic* of a transition of a molecule from a lower translational (t), or rotational (r), or vibrational (v) energy level to a considerably higher level of the same kind of motion.

The energy differences between levels in a truly accurate depiction would be quantized from specific spectral lines. Yet, Figure 1 is even more profoundly inaccurate than its arbitrary line spacing. Modern descriptions of molecular energetics come from quantum mechanics and the Schrödinger equation. Wave functions of the Schrödinger equation for molecules that are quantified in microstates inseparably combine two disparate qualities: energy, *and the probability of po-*

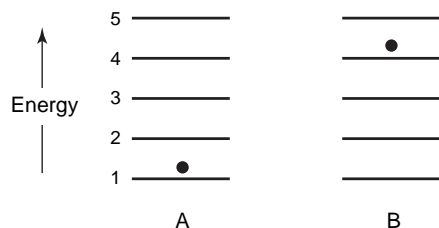[†]Professor Emeritus, Occidental College, Department of Chemistry, Los Angeles, CA 90041.

Figure 1. Microstate (single-particle) at (A) lower temperature and (B) higher temperature.
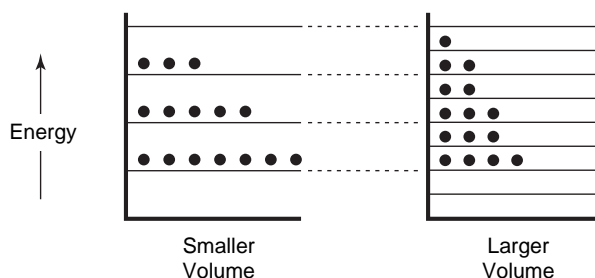


Figure 2. Microstate (multi-particle) in a smaller volume compared to an equal energy microstate of the same system in a larger volume. The original energy becomes more dispersed.

*sition in space* of the molecules. Thus, although Figure 1 could be said to represent microstates, it is not an adequate schematic because it shows only energy relationships; it *omits the absolutely non-separable space occupation* that is integral in the mathematics.

Therefore, Figure 1A and B, an attempt to show the energy change between two microstates, is really only symbolic of microstates because the likelihood of locations in space of the molecule is not shown. (The location is tacitly unchanged between A and B.) With this omission understood in any such diagram of a microstate, Figure 1A can be considered as the microstate of a molecule at a moderate temperature with t, r, and v total energies corresponding to a quantum energy level, arbitrarily numbered 1. The molecule cannot "access" the higher quantum levels arbitrarily numbered 2 to 5 (i.e., they are not "available" to it) because the molecule's energy simply is not great enough to correspond to those levels. However, if the single-molecule system of 1A is heated, the additional energy—dependent on the quanta involved—allows the molecule's energy to be on any one of the several higher energy quantum levels 2 to 5, including that shown in Figure 1B. With the addition of energy, those variations of Figure 1B are then said to be available or accessible or occupiable microstates.

Although it is symbolic only of a single particle's behavior, the example below can serve as a guide to what happens in the enormous group of molecules in a macro system. When a mole of a substance is heated, the $10^{23}$ molecules (~N) are able to access many microstates that they could not before. This is *why* energy so readily disperses in substances that are cooler than their warm surroundings: there is such an enormously greater number of microstates possible in the cooler material that the energy transferred to its molecules can "access" and thereby become more spread out.

> *Example.* When one mole of water at 273 K is warmed by its surroundings just to 274 K, there is an increase of $10^{10,000,000,000,000,000,000,000}$ ($10^{0.01N}$) *times* the number of microstates in the 273 K water—whose macrostate itself corresponds to an incomprehensible 10 to an exponent with 24 zeros ($10^{3.3N}$) of microstates. (Such enormous numbers of microstates can best be sensed comparatively as exponents denoted by a power in *N*.)

According to Boltzmann's relationship, $S = k_B \ln W_{max}$ (or $\Omega$), where $k_B$ is Boltzmann's constant and $W_{max}$ (or $\Omega$) is the count of how many microstates correspond to the par-

ticular macrostate. Because the number of microstates determines the number of ways that the total energy of a macrostate can be spread out, any change that leads to a greater number of microstates means that there is greater dispersion of the energy in a system, that is, an increase in its entropy.

Therefore, when a substance is heated, its entropy increases because the energy acquired and that previously within it can be far more dispersed than before among the many newly accessible microstates associated with the molecules of the substance. A simplified statement would be that there are many more microstates available for energy dispersal. (The common comment "heating causes or favors molecular disorder" is an anthropomorphic labeling of molecular behavior that has more flaws than utility) (*1*).

When the volume of a gas is increased by isothermal expansion into a vacuum, an entropy increase occurs, although not for the same reason as when a gas or other substance is heated. There is no energy change in such an expansion of the gas; d*q* is zero. Instead, there is an increase in the *density* of the microstates in the gas. As symbolically shown in Figure 2, when a gas expands into a vacuum, the number of microstates increases in any small energy range of the original volume when a larger volume is available. For those molecules whose energy is associated with that particular energy range, this results in an increased dispersion of their original energy because it can now be spread out to a greater number of microstates than before the gas expanded. Because of such an increase in energy dispersal, the entropy of the system increases. Entropy increases as volume increases—but *not* simply because there is more space for the molecules!

When two dissimilar ideal gases or liquids mix, the same phenomenon pertains as that for gas expansion: There is an increase in entropy because of the increased density of microstates in the larger volume available to each. Each substance can spread the energy associated with its molecules more widely, among more microstates.

## Simple Entropy Changes

### The Entropy of a Substance at a Temperature, T

The entropy of a substance at any temperature *T* is not complex or mysterious. It is simply a measure of the total quantity of energy that had to be dispersed within the substance from 0 K to *T* so the substance could exist as a solid or liquid or gas at the designated temperature. Because the
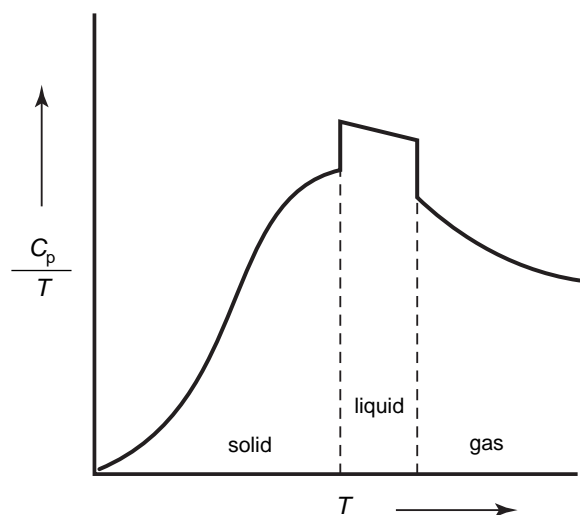
Figure 3. The $C_p/T$ vs $T$ from 0 K for a substance. The area under the curve (plus $q/T$ at any phase change) is the entropy of the substance at $T$.

heat capacity at a given temperature is the energy dispersed in a substance per unit temperature, integration from 0 K to $T$ of $\int C_p/T\,dT$ (+ $q/T$ for any phase change) yields the total entropy. This result, of course, is equivalent to the area under the curve to $T$ in Figure 3.

### Phase Change: Fusion and Vaporization

To change a solid to a liquid at its melting point requires a large quantity of energy to be dispersed from the warmer surroundings to the equilibrium mixture. This energy transfer is needed for the existence of the liquid state because of the far greater number of microstates of rotation and translation among which energy can and *must* be spread out than in the solid. The fusion process is isothermal (unlike warming a solid below its melting point) until a sufficient number of microstates in the equilibrium mixture correspond to the liquid macrostate and all solid has been converted to liquid. The entropy increase in this isothermal dissipation of energy from the surroundings is $\Delta H_{\text{fusion}}/T$. Similar considerations of increasing the number of accessible microstates apply to changing a liquid at its boiling point to a vapor: this requires energy dispersal from the surroundings to the liquid at an entropy increase of $\Delta H_{\text{vaporization}}/T$.

### The Expansion of a Gas into a Vacuum. The Mixing of Ideal Fluids.

The entropy effects in gas expansion into a vacuum, as described previously, are qualitatively similar to gases mixing or liquids mixing. The original energy of a constituent can be more dispersed in the new larger volume because the density of its microstates increases and therefore more microstates become accessible. Thus, the process is spontaneous and the entropy increases *(5, 6)*. As Craig has well said, "The 'entropy of mixing' might better be called the 'entropy of dilution'" *(7a)*. Meyer vigorously pointed toward this, stating that "the spontaneity of processes generally described as 'mixing', that is, combination of two different gases initially *each* at pressure, *p*, and finally at *total* pressure, *p*, has *abso-*

*lutely nothing* to do with the mixing itself of either" (*8,* italics as in the original). Ideal gases or liquids mix spontaneously in their combined greater volumes because then their original energy is more dispersed in the new situation of more dense microstates. Their entropy increases.

### Colligative Properties

"Escaping tendency" or chemical potential involving graphs that are complex to a beginner are often used to explain the freezing point depression and boiling point elevation of solutions. These topics can be far more clearly discussed by first describing the entropy change that occurs when non-volatile solutes are added to a solvent. Parallel to the increase in the density of microstates and thus their greater accessibility when one fluid is mixed with another, the microstates of solvent molecules in a solution are more dense than those of the pure solvent. Thus, in a solution a solvent's energy is more dispersed and its entropy is increased as compared to the pure solvent. (This is the fundamental basis for a solvent's decreased "escaping tendency" when it is in a solution. If the energy within the solvent in a solution is less localized, more spread out, the solvent tends less to escape to another phase.)

Consider a most common example of water: Because of its greater entropy in a solution, liquid water containing a solute that is insoluble in ice is not at equilibrium with solid ice at 273 K. Somehow, the more-dispersed energy in the water of the solution must be decreased for the water to change to ice. Although the cause of the greater dispersion—the increased density of solvent microstates in the solution—cannot be altered, the accessibility or occupancy of those microstates can be decreased by decreasing the energy of the water molecules. Lowering the temperature of the surroundings causes energy *from* the solution to be dispersed *to* the surroundings. When that is done, the decrease in energy in the solution compensates for the greater spreading out of the water's energy in the solution, and the water reaches thermodynamic equilibrium for crystallization to ice at a lowered temperature. As energy (the enthalpy of fusion) continues to be dispersed to the surroundings, the liquid water freezes.

The elevation of boiling points of solutions having a non-volatile solute is as readily rationalized as is freezing point depression. The more dispersed energy (and greater entropy) of a solvent in the solution means that the expected thermodynamic equilibrium (the equivalence of the solvent's vapor pressure with atmospheric pressure) cannot exist at the solvent's normal boiling point. For example, the energy in water in a solution at 373 K is more widely dispersed among its microstates than is pure water at 373 K. There is a lesser tendency for water molecules to leave a solution for the vapor phase than from pure water. Energy must be transferred from the surroundings to an aqueous solution to increase its energy content, thereby compensating for the greater dispersion of the water's energy due to its being in a solution, and raise the vapor pressure of that water in the solution. As energy is dispersed to the solution from the surroundings and the temperature rises above 373 K, at some point a new equilibrium temperature for phase transition is reached. Because the vapor pressure of the water in the solution now equals the atmospheric pressure, the solvent water boils.

## Osmosis

Although the hardware system of osmosis is unique, the process that occurs in it is merely a special case of volume increase via mixing that has been discussed. From a molecular viewpoint, mixing a pure solvent with a solution results in denser microstates for the solvent molecules and thereby its energy dispersion is increased. Greater energy dispersal is measured by an increase in entropy. If a semi-permeable membrane with solvent on one side passes only solvent into a solution on its other side, that movement is spontaneous because it is entropically favored. The solvent will increase in entropy if it flows to the solution side of the membrane.

## More-Complex Entropy Change

The following section discusses a general view of spontaneous chemical reactions wherein energy changes occur in chemical bonds that disperse energy in the surroundings.

### The Gibbs Function, an All-Entropy Equation of State

Undoubtedly, the first-year chemistry texts that directly state the Gibbs equation as $\Delta G = \Delta H - T\Delta S$, without its derivation involving the entropy of the universe, do so in order to save valuable page space. However, such an omission seriously weakens students' understanding that the "free energy" of Gibbs is more closely related to entropy than it is to energy (9). This quality of being a very different variety of energy is seen most clearly if it is derived as the result of a chemical reaction in a constant pressure, constant temperature system doing only $PV$ work as is shown in some superior texts, and developed below.

If there are no other events in the universe at a particular moment that a spontaneous chemical reaction occurs in a system, the changes in entropy are: $\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$. However, the internal energy evolved from changes in bond energy, $-\Delta H$, in a spontaneous reaction in the system passes to the surroundings. This $-\Delta H_{system}$, divided by $T$, is $\Delta S_{surroundings}$. Inserting this result (of $-(\Delta H/T)_{system} = \Delta S_{surroundings}$) in the original equation gives $\Delta S_{universe} = -(\Delta H/T)_{system} + \Delta S_{system}$. But, the only increase in entropy that occurred in the universe initially was the dispersal of differences in bond energies as a result of a spontaneous chemical reaction in the system. To that dispersed, evolved bond energy (that therefore has a negative sign), we can arbitrarily assign any symbol we wish, say $-\Delta G$ in honor of Gibbs, which, divided by $T$ becomes $(-\Delta G/T)_{system}$. Inserted in the original equation as a replacement for $\Delta S_{universe}$ (because it represents the total change in entropy in the universe at that instant): $-(\Delta G/T)_{system} = -(\Delta H/T)_{system} + \Delta S_{system}$. Finally, multiplying the whole by $-T$, we obtain the familiar Gibbs equation, $\Delta G = \Delta H - T\Delta S$, all terms referring to what happened or could happen in the system.

Strong and Halliwell rightly maintained that $-\Delta G$, the "free energy", is not a true energy because it is not conserved (9). Explicitly ascribed in the derivation of the preceding paragraph (or implicitly in similar derivations), $-\Delta G$ is plainly the quantity of *energy that can be dispersed to* the universe, the kind of entity always associated with entropy increase, and not simply energy in one of its many forms. Therefore, it is not difficult to see that $\Delta G$ is indeed *not* a true energy. Instead, as *dispersible energy*, when divided by $T$, $\Delta G/T$ is an entropy function—the *total* entropy change associated with a reaction, not simply the entropy change *in* a reaction, $S_{products} - S_{reactants}$, which is the $\Delta S_{system}$. That is why $\Delta G$ has enormous power and application, from prediction of the direction of chemical reaction, to prediction of the maximum useful work that can be obtained from it. The Planck function, $-\Delta G/T$, is superior in characterizing the temperature dependence of the spontaneity of chemical reactions *(10, 11)*. These advantages are the result of the power of the general concept of entropy itself and the relation of $\Delta G$ to it, not a result of $\Delta G$ being some novel variant of energy.

### Why Reactions Do Not Go to Completion: Why an Equilibrium State Has Increased Entropy Compared to a Completed Reaction (11)

A significant contribution to teaching is using entropy to explain quickly and simply why many chemical reactions that involve solutions or mixtures do not go to completion. ("Completion" is here used in the sense that no reactants remain after the reaction; products are formed in 100% yield.) Thus, the final destination of those many reactions is an equilibrium state containing both products and some unchanged reactants.

Many texts say something like "systems can achieve the lowest possible free energy by going to equilibrium, rather than proceeding to completion" and support the statement well by quantitative illustrations of the free energies of forward and reverse reactions. Few texts present a qualitative description of the entropy changes (which are essentially $\Delta G/T$ changes) that immediately simplify the picture for students.

As mentioned repeatedly in this article, mixtures of many types have higher entropy than their pure components (*not* caused by any profound or novel "entropy of mixing", but simply due to increased density of microstates with increased volume). Thus, students who have been shown examples of this phenomenon can immediately understand why, in a reaction of A to make B, the entropy of a mixture of B with a small residual quantity of A would be greater than that of pure B. Therefore, the products in many such reactions would more probably be such a mixture because this would result in a greater entropy increase in the reaction than formation of only pure B. The qualitative conclusion that reactions that are moderately exothermic go to an equilibrium of B plus some A rather than to completion readily becomes apparent on this basis of maximal entropy change, determined by $-R \ln K$, $(\Delta G°/T)$.[3]

## Summary

Energy associated with macro objects or with molecules disperses, spreads out, dissipates from being localized if the dispersal process is not hindered, for example by physical obstacles or by chemical activation energies or other barriers. In objects with kinetic or potential energy, that dispersion occurs via changes that ultimately warm the surroundings. Most frequently energy in molecules is dispersed by the energy becoming spread among a larger number of microstates than was the case in the original system.

This dispersal of energy gives direction to physical and chemical events and is the driving force for them. Energy's

dispersing is probabilistic rather than deterministic. As a consequence, there may be small sections of a larger system in which energy is temporarily concentrated. (Chemical substances having greater free energies than their possible products are examples. They continue to exist because of activation energies that act as barriers to instant chemical reaction and dispersion of their internal bond energies *[12]*.)

Entropy change is the index of the dispersion of energy at a temperature $T$. Entropy is not disorder, not a measure of disorder, not a driving force. The entropy of a substance, its entropy change from 0 K to any $T$, is a measure of the energy that can be dispersed within the substance at $T$: integration from 0 K to $T$ of $\int C_p/T \, dT$ (+ $q/T$ for any phase change).

A molecular view of entropy is most helpful in understanding entropy change. Microstates are quantum mechanical descriptions of ways that molecules can differ in their energy distribution and probable location; an enormous number of microstates correspond to any macrostate above 0 K. When a macrostate is warmed, a greater dispersal of energy can occur in a substance or a system because additional microstates become accessible. This increased spreading out of energy is reflected in the entropy increase per unit of temperature. Liquids have hugely greater numbers of microstates than their solid phase at the same temperature because of the additional microstates made available in translational and rotational and some vibrational modes. Further great increases in accessible microstates become available in these modes in vapor phases. Greater dispersal of energy is indicated by an increase in entropy of these phases from 0 K.

Gas expansion into a vacuum, mixing of ideal gases or liquids, diffusion, colligative effects, and osmosis each fundamentally involves an increase in entropy due to increased dispersion of energy (with no change in total energy in the case of ideal fluids) in more dense microstates.

At its heart, the Gibbs equation is an "all-entropy" equation of state. The Gibbs energy has been accurately criticized as not "a true energy". It is not conserved. The Gibbs energy, $-\Delta G$, can be correctly described as "dispersible energy" rather than a variety of energy, because of its ultimate definition as the energy portion of an entropy function, $-\Delta G/T$. Modestly exothermic reactions go to equilibrium rather than to completion because a mixture of substances has a larger entropy than a pure substance. Highly exothermic reactions proceed essentially to completion because the thermal transfer to the surroundings constitutes an overwhelmingly greater entropy change than any minute counter from the mixing of products with reactants in the system.

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## Notes

1. Though constrained by the knowledge of their day, Kelvin (W. Thomson) still called the flow of energy from a hot to a cold body a "dissipation of energy" (*13*) while Clausius' "change in disgregation value" (*14*) led to entropy that Barón summarizes as

"a measure of the capacity energy may have to flow from one place of the universe to another" (*15*). Far more recently, Lowe (*16*), Craig (*7b*), Atkins (*17, 18*) and Bindel (*19*) range from an occasional mention to frequent use of energy dispersal as the basis for understanding entropy change. Leff provides thorough theoretical support for interpreting entropy increase as increased energy dispersal among molecular microstates (*3a, b*).

2. "Energy" in this article will mainly refer to the potential and kinetic energy in molecules and chemical systems in two principal categories: (1) the bond energies within molecules (internal chemical energy), and (2) the energy associated with molecular motions of all types (translational, rotational, vibrational). (Category (2) has been called the "thermal energy" of molecules. However, Craig points out that "thermal energy is an energy content" and "thermal energy" should not be used in describing an energy transfer process (*20*). Therefore, in this article when energy associated with molecular motion is transferred, the single word "energy" is used in discussing the transfer.)

Before focusing on chemical systems for a class of beginners, the instructor can profitably illustrate the spontaneous dispersal of energy as a common phenomenon in everyday happenings. This can be wide in scope, including a bouncing ball ceasing to bounce, the results of a car crash (kinetic energy dispersed to twisted warm metal, etc.), highly charged clouds (yielding lightning bolts), attenuation effects with which students are familiar (loud musical sounds a room or dormitory away), or ripple heights (from an object thrown in a swimming pool). All forms of energy associated with common objects as well as with molecules become more dissipated, spread out, dispersed *if there are ways in which the energy can become less localized* and the dispersal process is not hindered. (In the case of molecules where energy must be considered quantized these ways of becoming less localized are described as accessible microstates.)

3. A novel example of $NO_2$ forming $N_2O_4$ gives details of the influence of entropy in yielding an equilibrium mixture rather than a pure $N_2O_4$ product (*21*).

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